An Investigation of the Mechanism and Stereochemistry of the Peterson Reaction

Thesis

An Investigation of the Mechanism and Stereochemistry of the Peterson Reaction

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By

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DECLARATION

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ABSTRACT

The Peterson reaction is a method of carbonyl olefination and may be regarded as the silicon analogue of the Wittig reaction. The main purpose of this project has been to try to determine how the stereochemistry of the Peterson reaction may be affected by changing reaction conditions and changing the groups about the silicon atom.

The results obtained show that the stereochemistry of the Peterson reaction is largely unaffected by performing the reaction in different solvents, at different temperatures, in the presence of inorganic salts and with different counterion ions. However, placing sterically bulky groups about the silicon atom causes an increase in the proportion of *cis* olefin being produced.

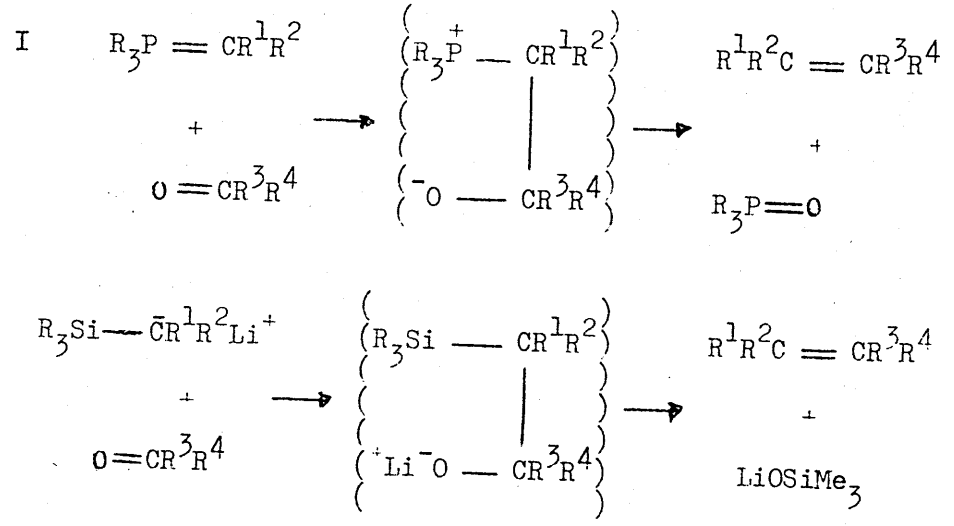
M.N.D.O. calculations have also been performed in order to determine the nature of an α-silyl carbanion and to determine the importance of silicon oxygen interaction in the intermediate of the Peterson reaction.

Chapter 1 INTRODUCTION

1.1 The Formation and Structure of Phosphoranes

The Peterson reaction[1], like the Wittig reaction[2], is a method of introducing a carbon-carbon double bond at the position of a carbonyl group in an organic molecule. As such a brief survey of the literature related to the Wittig reaction may give valuable insight into the mechanism, kinetics and stereochemistry of the Peterson reaction. A comparison of the Wittig and Peterson reactions is given in Scheme 1.

Scheme 1.



Possible intermediates

in both cases

Phosphorus ylids I may be described as stabilized, semi-stabilized or non stabilized. Stabilized ylids have electron withdrawing substituents, such as $-CO_2R$, $-COC_6H_5$ or -CN alpha to the carbanion which can delocalize the negative charge. They do not react with oxygen or water and can be generated using a weak aqueous base, (equation 1).

$$X^- \; R_3\overset{+}{P}CH_2CO_2R^1 \xrightarrow{\bar{O}H(aq)} R_3P{=}CHCO_2R^1 \quad (1)$$

The effect of the stabilizing group on the formation of the corresponding phosphorus ylids can be appreciated by examining the pKas of a series of phosphonium salts.[3] Typical results are given in Table 1.

Table 1. The effect of stabilizing groups on the ease of formation of Phosphorous Ylids

Phosphonium salt	Order of pKa's for a series of salts
$Ph_3\overset{+}{P}CH_2COR\ X^-$	$R = 4\text{-}NO_2C_6H_4 < C_6H_5 < 4\text{-}CH_3OC_6H_4$ $R = ClCH_2 < CH_3 < CH_3OCH_2 < H_2NCH_2$

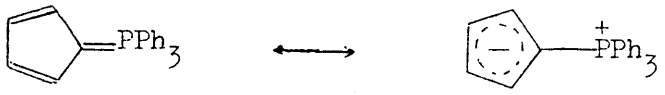
Non stabilized ylids have aliphatic side chains which allow little delocalization of the negative charge of the carbanion. They react with oxygen and water and are generated using a strong base (equation 2).

$$X^- \; R_3\overset{+}{P}CH_2R^1 \xrightarrow{C_6H_5Li} R_3P{=}CH_2R^1 \quad (2)$$

Semi stabilized ylids have groups such as aryl, alkenyl or alkynyl attached to the carbanionic carbon and have intermediate properties, being able to delocalise the negative charge to some extent.

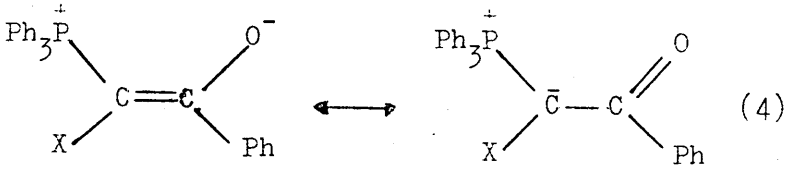
The i.r. spectra of many phosphorus ylids display a band between 1200 and 1220cm^{-1} assigned as a P=C stretching vibration.[4] The u.v. spectra of ylids exhibit a broad band between 300 and 400nm due to a $\pi-\pi^*$ transition of the P=C bond[5]. Tailing of this band into the visible is probably responsible for the yellow colour of ylids.

Dipole moments also provide evidence for double bond character in ylids. The experimental dipole moment for tryphenylphosphonium-cyclopentadienylid II,[6,7] was 23×10^{-23} Cm and lies halfway between the calculated values for the structures in equation 3. This suggests a 50% contribution from each canonical form.

II  (3)

$\mu = 0$ $\mu = 47 \times 10^{-23}$ Cm

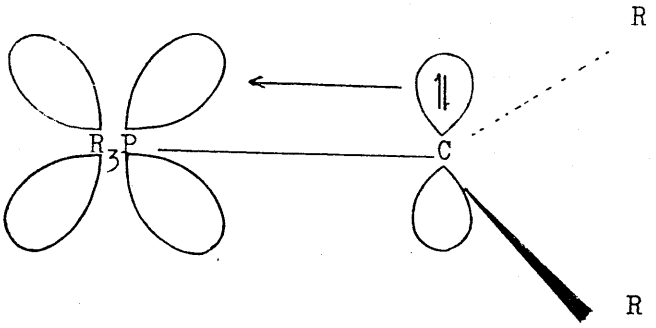
X-Ray diffraction analyses have been carried out on a number of ylids. Data for the stabilized ylid III show that the molecule is planar with

III  (4)

X = Cl, I

two sp^2 hybridized carbons and that the phosphorus and oxygen atoms are Z to one another. The carbon phosphorus bond length (171-174pm)[8] is midway between that of a single and a double bond. The structure of methylenetriphenylphosphorane has also been established by X-ray analysis,[9-12] and in this case the carbon phosphorus bond length is quite short (166pm) being close to the sum of the double bond radii of phosphorus and carbon.

The best description of bonding in a phosphonium ylid involves electron donation from the doubly occupied carbon p-orbital into a vacant d-orbital of the phosphorus. The extent of overlap between the p and d orbital will be affected by substituents on carbon and phosphorus.[13]



IV

d-orbitals p-orbitals

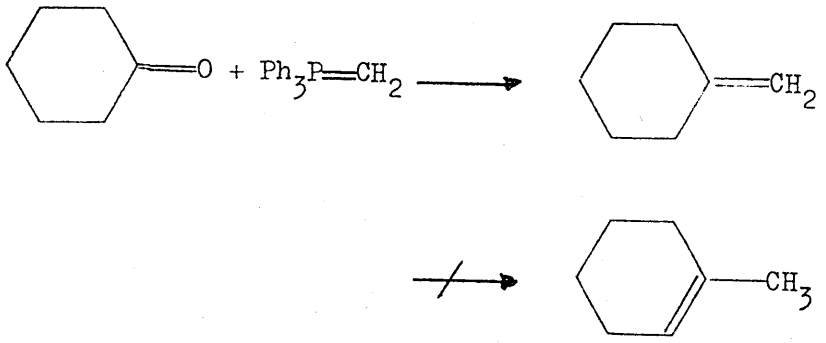
1.2 The use of the Wittig Reaction in synthesis

A detailed study of the use of phosphorus ylids in carbonyl olefination was initiated by Wittig and Geisler[2] in 1953, who found the reaction of methylenetriphenylphosphorane with benzophenone produced triphenylphosphine oxide and diphenyl ethylene in 84% yield. However, this was not the first of this type of reaction to be carried out. As early as 1919,[14,15] Staudinger reacted benzhydrylidenetriphenylphosphorane with phenylisocyanate to give triphenylketenimine.

The Wittig reaction is now used widely throughout organic chemistry. The carbonyl moiety may be an aliphatic, alicyclic or aromatic aldehyde or ketone. Other functional groups do not generally interfere; the carbonyl component may contain double or triple bonds, hydroxy, alkoxy, amino, halo and even ester groups. Although phosphorus ylids do react with esters the reaction is generally too slow to compete with the reaction with aldehydes or ketones. The ylid component may also contain double and triple bonds and other functional groups. However, unstabilized ylids are very reactive and besides reacting with carbonyl compounds they react with water, oxygen, carbon dioxide and alcohols. Reactions employing non-

stabilized ylids must therefore be carried out in the absence of these compounds.

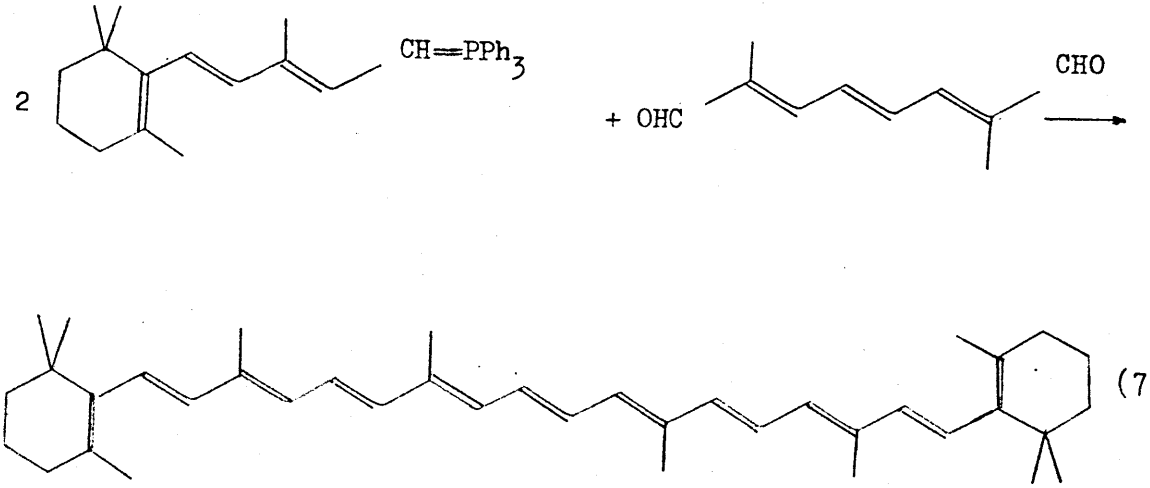
The Wittig reaction is particularly useful for ensuring the specific location of a double bond. This can be illustrated by the preparation of methylenecyclohexane (equation 5) free from the thermodynamically more stable endocyclic isomer[16] and by the preparation of β,γ unsaturated acids[17] (equation 6).



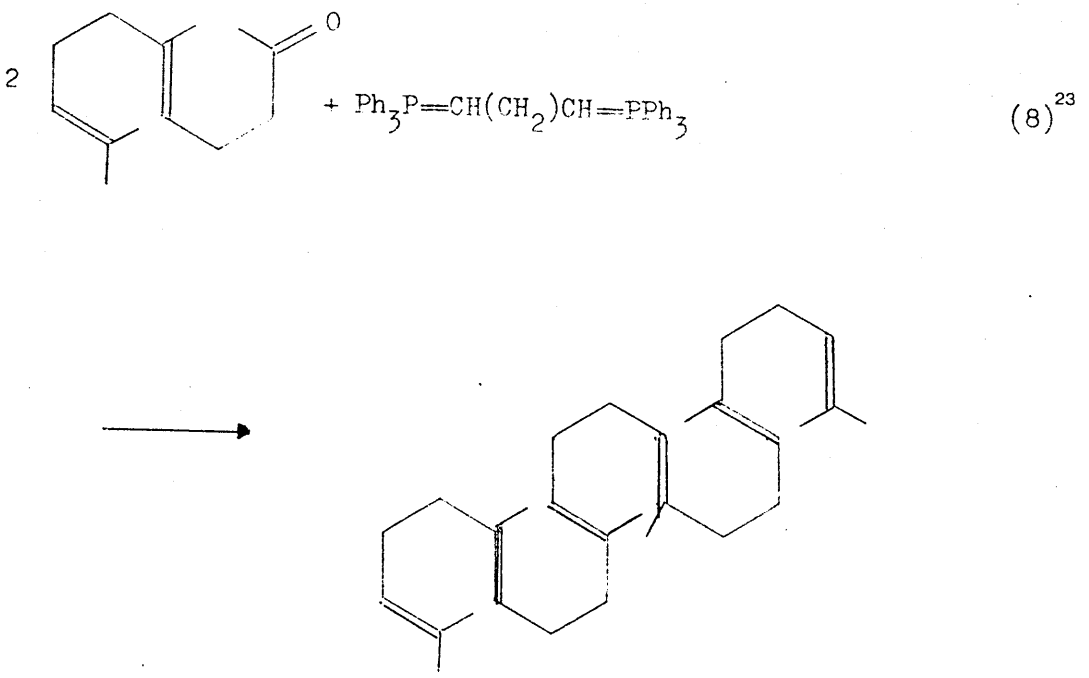
(5)

$$Me_2C{=}O + Ph_3P{=}CHCH_2CO_2^- \longrightarrow Me_2C{=}CHCH_2CO_2^- \qquad (6)$$

The Wittig reaction has also proved to be very successful in the synthesis of natural products,[18,19] particularly polyenes.[20,21] Surmatis and Hofner used this reaction to synthesize β-carotene[22] (equation 7) and Trippett prepared the first pure sample of all trans-squalene[23] by the condensation of geranyl acetone with a bis ylid (equation 8).



(7)[22]



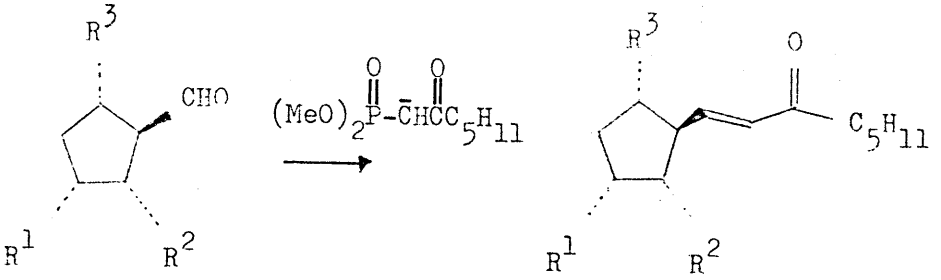
(8)[23]

The Wittig reaction was further developed by Horner[24,25] to include carbanions generated from phosphonates using strong bases such as sodium hydride. These carbanions are more reactive than conventional ylids and when R^2 and R^3 (equation 9) are electron withdrawing they will react with ketones, whereas the corresponding ylids are often inert. The phosphorus-containing reaction product is a water soluble phosphate ester, which makes separation from the olefin much easier. When diastereomeric alkenes are produced the product is always predominantly <u>trans</u>.[26]

$$(R^1O)_2\overset{O}{\overset{\|}{P}}CHR^2R^3 \xrightarrow{NaH} (R^1O)_2\overset{O}{\overset{\|}{P}}\bar{C}R^2R^3 \xrightarrow{R^4R^5C{=}O} (R^1O)_2PO_2^- + R^2R^3C{=}CR^4R^5 \qquad (9)$$

This reaction is known as the 'Horner-Emmons' reaction and is extensively used in the preparation of the C_8 <u>trans</u> olefin side chain

of prostaglandins (equation 10).[28,27]

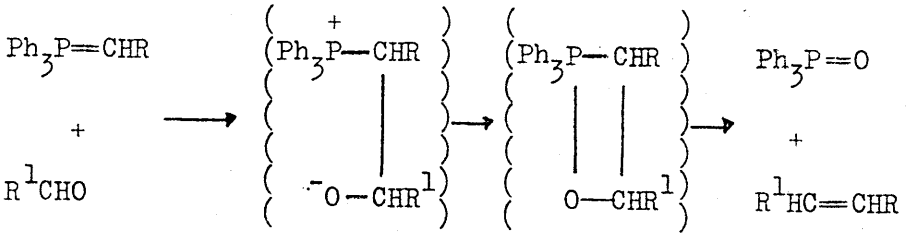


(10)

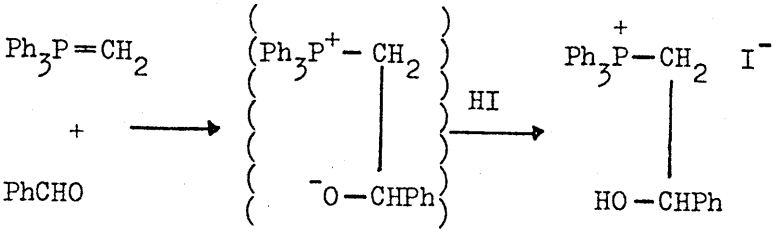
1.3 The Mechanism of the Wittig Reaction

The mechanism of the Wittig reaction has been investigated by several groups of research workers for many years. Initially it was proposed[3,29-31] that phosphorus ylids and carbonyl compounds react to form an intermediate betaine which underwent ring closure to an oxaphosphetane followed by decomposition to give olefin and phosphine oxide as illustrated in Scheme 2.

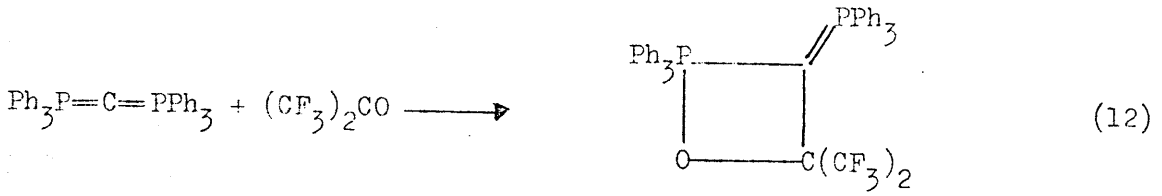
Scheme 2



In some cases the intermediate betaine has been trapped out by protonation[32] and in one special case an oxaphosphetane has been isolated and characterized.[33] These intermediates are illustrated in equations 11 and 12.



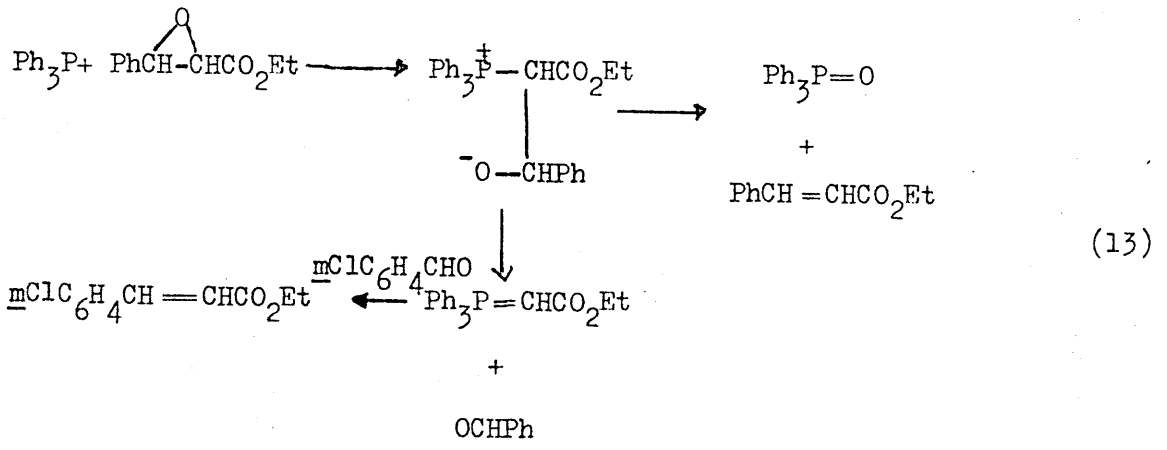
(11)



(12)

Speziale and Bissing[34] proposed four distinct mechanisms for the Wittig reaction. These were: (a) rapid, irreversible betaine formation and its rate-controlling decomposition to products; (b) slow, irreversible formation of betaine and rapid decomposition of betaine to products; (c) rapid, reversible betaine formation and rate-determining formation of olefin; (d) slow, reversible betaine formation with rapid decomposition of betaine to phosphine oxide and olefin.

The Wittig reaction has been shown to be reversible to some extent for stabilized, semi-stabilized and non-stabilized ylids.[35,36] For example, ethyl m-chlorocinnamate was formed when triphenylphosphine was reacted with cis or trans ethylphenylglycidate in the presence of m-chloro-benzaldehyde as illustrated in equation 13.

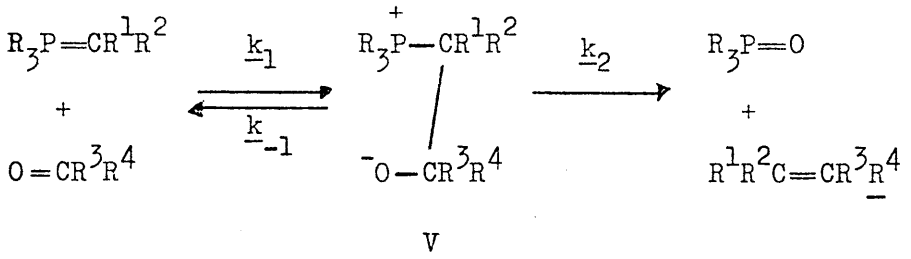


(13)

Hence mechanisms (a) and (b) can be disregarded, at least in this particular case.

Mechanisms (c) and (d) can be represented by the mechanistic scheme given below. Mechanism (c) implies that $\underline{k}_{-1} > \underline{k}_2$ and mechanism (d) implies that $\underline{k}_1 < \underline{k}_2$ and $\underline{k}_{-1}$ and that $\underline{k}_2 \gg \underline{k}_{-1}$.

Scheme 3.



V

Application of the steady state approximation to the above scheme gives the following rate equations.

$$\frac{d[R^1R^2C{=}CR^3R^4]}{dt} = \underline{k}_2 \cdot [V] \qquad (14)$$

As V is a reactive intermediate, that is its concentration will be small and hardly change during the reaction, the equation below can be set to zero. Thus it is possible to determine [V] and hence the rate equation.

$$\frac{d[V]}{dt} = \underline{k}_1[R_3P{=}CR^1R^2]\,[O{=}CR^3R^4] - \underline{k}_{-1}[V] - \underline{k}_2[V] = 0 \qquad (15)$$

$$\therefore\ [V] = \frac{\underline{k}_1}{\underline{k}_{-1} + \underline{k}_2}\,[R_3P{=}CR^1R^2]\,[O{=}CR^3R^4] \qquad (16)$$

$$\frac{d[R^1R^2C{=}CR^3R^4]}{dt} = \frac{\underline{k}_2\underline{k}_1}{\underline{k}_{-1} + \underline{k}_2}\,[R_3P{=}CR^1R^2]\,[O{=}CR^3R^4] \qquad (17)$$

To determine whether mechanism (c) or (d) was operating, Speziale and Bissing[36] studied the reaction of carboethoxymethylene-triphenylphosphorane with a series of para and meta substituted aldehydes. The results they obtained are illustrated in Table 2. They found that the kinetics of these reactions were second order and the rate of disappearance of ylid was the same as the rate of formation of the olefin. They also measured the entropy of activation, $\Delta S^{\neq}$, by carrying out experiments at 25°C and 45°C and obtained a value of $170 JK^{-1}mol^{-1}$.

The effect of substitution in the aldehyde on the order of rate constants was p-NO_2 > m-Cl > p Cl > H > p-Me > p-MeO giving a good Hammett correlation against σ with a ρ value of +2.7.

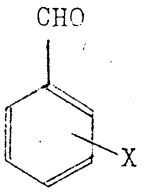
Mechanism (c) involves the rapid reversible formation of a betaine and rate determining formation of olefin and phosphine oxide. Hence ρ reflects all the rate constants k_1, k_{-1} and k_2 and the net effect of p-substitution would be small and unpredictable. Mechanism (d) involves the slow reversible formation of a betaine and rapid decomposition to olefin and phosphine oxide. Dividing rate equation (17) by k_2 gives equation (18). Assuming the ratio k_{-1}/k_2,

$$\frac{d\left[R^1R^2C{=}CR^3R^4\right]}{dt} = \frac{k_1}{(k_{-1}/k_2)+1}\left[R_3P{=}CR^1R^2\right]\left[O{=}CR^3R^4\right] \qquad (18)$$

remains constant with respect to substitution then ρ reflects solely k_1. Hence the observed ρ value of +2.7 is consistent with a developing negative charge at the oxygen in the transition state of the first step.

The effect of solvent polarity upon the reaction rates can also be mechanistically indicative. The reaction of ylids and aldehydes was

Table 2.

Kinetic data on the reaction of $(C_6H_5)_3P{=}C(Y)CO_2CH_3$ with 

X	Y	Temp ± 0.05°C	Solvent	$k_{obs} \times 10^4$ L mol^{-1}sec^{-1}
p-CH_3O	H	25.0	Benzene	0.71 ± 0.000
		45.0	Benzene	2.36 ± 0.02
		25.0	Chloroform	4.35 ± 0.02
		25.0	Methanol	657.0 ± 3.0
p-CH_3	H	25.0	Benzene	2.15 ± 0.03
		45.0	Benzene	6.69 ± 0.04
		25.0	Chloroform	12.4 ± 0.3
p-H	H	25.0	Benzene	9.62 ± 0.02
		45.0	Benzene	28.6 ± 0.4
		25.0	Chloroform	43.6 ± 0.4
	Cl	25.0	Benzene	5.75 ± 0.02
	Br	25.0	Benzene	1.85 ± 0.01
p-Cl	H	25.0	Benzene	24.5 ± 0
		45.0	Benzene	67.1 ± 0.3
		25.0	Chloroform	124 ± 1
m-Cl	H	25.0	Benzene	120 ± 4
p-NO_2	H	25.0	Benzene	1060 ± 0.00

5-6 times faster in chloroform than in benzene and about 1000 times faster in anhydrous methanol than in benzene. Assuming k_{-1}/k_2 is again constant with respect to solvent then the effect of solvent on the reaction would be solely reflected by k_1. The charged intermediate betaine produced by the reaction of ylid and aldehyde would be stabilized by protic solvents. Hence the increased rate of reaction in protic solvents is consistent with mechanism (d).

Further evidence in support of mechanism of (d) was obtained by adding tertirary phosphines to cis and trans ethyl phenylglycidate in the presence of m-chlorobenzaldehyde as illustrated in Table 3.

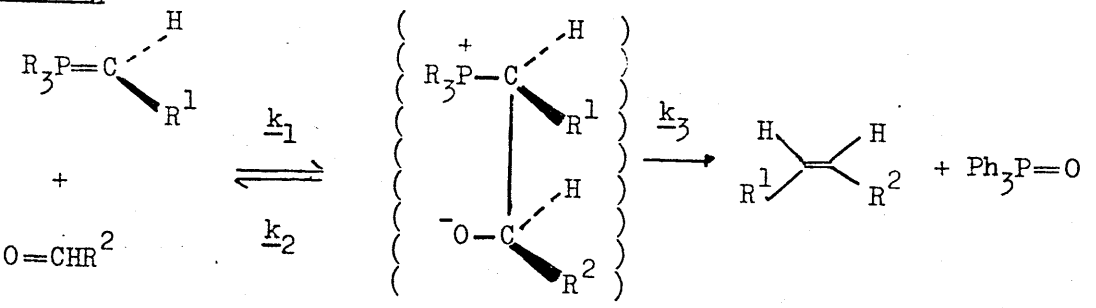
Table 3. The stereochemical outcome of reactions between $R_3P(x)$, $C_6H_5CH—CHCO_2Et$ (y) and $m\text{-}ClC_6H_4CHO(z)$

R	Nature of Epoxide	Relative Concentration x:y:z	Product olefins %			
			$C_6H_5CH=CHCO_2Et$		$m\text{-}ClC_6H_4CH=CHCO_2Et$	
			cis	trans	cis	trans
C_4H_9	trans	1:1:3	0	53.2	0	46.8
C_4H_9	trans	1:1:1	0	53.6	0	46.4
C_4H_9	cis	1:1:3	0	92.4	0	7.6
C_6H_5	trans	1:1:3	49.1	17.4	3.0	30.5
C_6H_5	trans	1:1:1	48.7	17.4	3.0	30.9
C_6H_5	cis	1:1:3	1.2	85.8	1.2	11.8

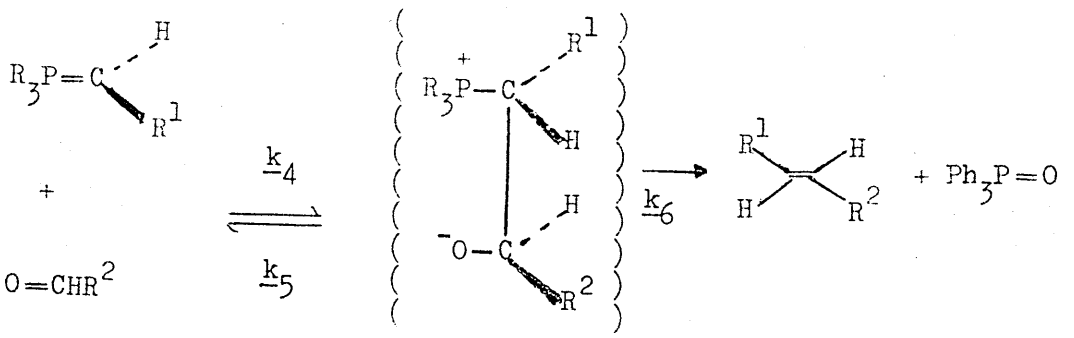
On the basis of the relative amount of substituted and unsubstituted olefin obtained it is possible to discount mechanism (c). If mechanism (c) were in operation and betaine formation was rapidly reversible, less ethyl cinnamate than ethyl m-chlorocinnamate would be expected since any ylid produced by decomposition of betaine would react preferentially with the more reactive m-chlorobenzaldehyde to give ethyl m-chlorocinnamate. However, experimentally the opposite trend was observed. These results can be explained by mechanism (d) involving slow reversible betaine formation since more ethyl cinnamate was produced than ethyl m-chlorocinnamate.

Further insight into the mechanism of the Wittig reaction can be gained by considering the reactions of unsymmetrically substituted phosphorus ylids with aldehydes which yield a mixture of cis and trans olefins. Trippet[37,38] proposed that the competing reactions leading to di-substituted cis and trans olefins could be represented in terms of Scheme 4 and that the ratio of isomers formed is given by equation (19). The synperiplanar conformation would be favoured due to attraction between the oppositely charged phosphorus and oxygen atoms.

Scheme 4.



VI



VII

$$\frac{[\underline{cis}]}{[\underline{trans}]} = \frac{\underline{k}_1(\underline{k}_5/\underline{k}_6 + 1)}{\underline{k}_4(\underline{k}_2/\underline{k}_3 + 1)} \qquad (19)$$

If $\underline{k}_1/\underline{k}_4 > 1$ and $\underline{k}_5/\underline{k}_6 > \underline{k}_2/\underline{k}_3$, the cis:trans ratio will be greater than one. Conversely, if $\underline{k}_1/\underline{k}_4 < 1$ and $\underline{k}_5/\underline{k}_6 < \underline{k}_2/\underline{k}_3$, the trans isomer will predominate. The ratios $\underline{k}_2/\underline{k}_3$ and $\underline{k}_5/\underline{k}_6$ which indicate the degree of reversibility were evaluated, using the results of Bissing,[35] for the reaction between phenylglycidate and triphenylphosphine in the presence of m-chlorobenzaldehyde and were found to be 0.5 and 0.15 respectively. The R_1 and R_2 groups of betaine VI are eclipsed and consequently VI is more sterically crowded than VII. $\underline{k}_1$ would therefore be expected to be less than $\underline{k}_4$. This coupled with the fact that $\underline{k}_2/\underline{k}_3 > \underline{k}_5/\underline{k}_6$ means the trans olefin will be preferred. The experimental cis:trans ratio produced by the reaction between carbethoxymethylene-triphenylphosphorane and benzaldehyde is 16:84. By inclusion of this value in equation (18) the value of $\underline{k}_1/\underline{k}_4$ can be calculated to be 0.25. These results indicate that both the rate of formation and the stability of the intermediate betaine can be major factors in determining the resultant stereochemistry of the olefin.

House[39] has investigated the effect of solvent and the addition of

lithium salts to the reaction of carbethoxymethylenetriphenylphosphorane with acetaldehyde. He found that the use of protic solvents or lithium salts increased the proportion of cis olefin produced relative to that produced in aprotic solvents. A similar increase in the proportion of cis olefin obtained in protic solvents was also noted by Lau who studied reactions between carbethoxymethylenetriphenylphosphorane and benzaldehyde. The results of House[39] and Lau[40] are given in Tables 4 and 5.

Table 4. The effect of lithium salts and solvent on stereochemistry of the reaction of carbethoxymethylenetriphenylphosphorane with acetaldehyde

CH_3CHO mmols	Ylid mmols	Solvent	Additives (mmols)	Yield (%)	Cis:Trans
4.3	0.97	CH_2Cl_2	-	84-88	6:94
5.5	9.1	DXE	-	90	3:97
4.3	1.06	DMF	-	95-98	3:97
4.3	0.90	CH_3OH	-	80-96	38:62
4.3	1.04	DMF	LiBr(1.28)	83-85	20:80
4.3	1.10	DMF	LiCl(1.24)	75-82	18:82
4.3	0.95	DMF	LiBr(4.8)	81	22:78
4.3	0.96	DMF	$LiClO_4$(0.90)	83	22:78
4.3	1.20	DMF	$LiClO_4 \cdot 3H_2O$(1.16)	70	20:80
4.3	0.90	CH_3OH	$LiNO_3$(7.40)	81	38:62
4.3	1.0	DMF	$LiNO_3$(1.0)	87	21:79
4.3	1.15	DMF	KCl(0.88)	82	4:96
4.3	0.99	DMF	$MgBr_2 \cdot 6H_2O$(1.08)	74	20:80
4.3	0.93	DMF	H_2O(0.95)	90	10:90
4.3	0.99	DMF	H_2O(28)	63	25:75
4.3	1.02	DMF	$C_6H_5CO_2H$(1.02)	85	4:96
4.3	1.01	CH_3OH	$C_6H_5CO_2H$(0.296)	83	34:66

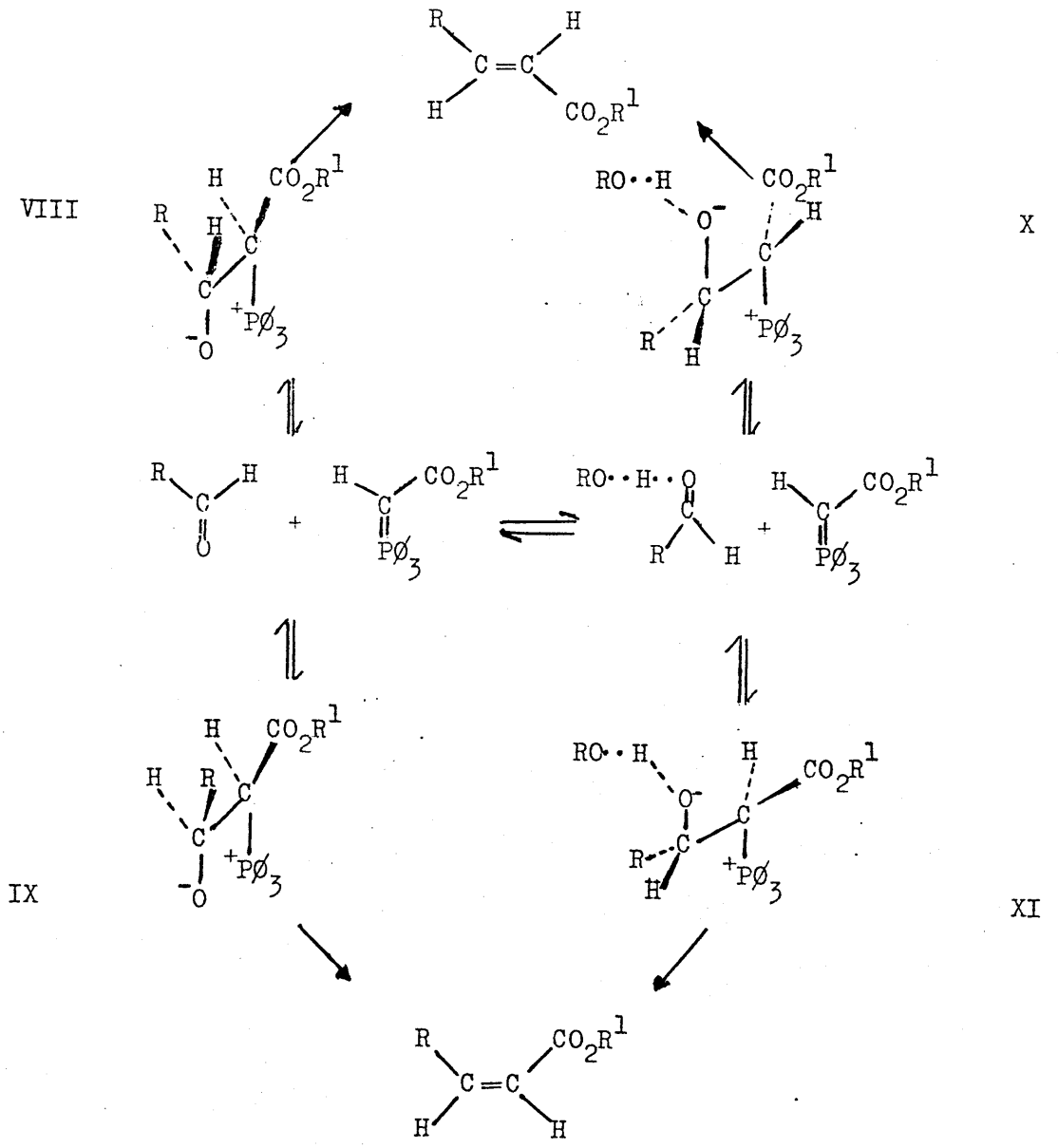
Table 5. The effect of solvent on the stereochemistry of the reaction of carbethoxymethylenetriphenylphosphorane with benzaldehyde

Solvent	% Cis Olefin	% Yield
CH_2Cl_2	3	100
Benzene	4	94
Dioxane	5	93
DMF	5	99
THF	5	83
CH_3CN	6	94
Ethanol	15	92
90/10 Dioxane/H_2O	26	41

These results were explained[39] by proposing that Lewis acids, such as methanol, water or lithium salts, coordinate with the oxygen of the betaine, affecting the stereochemistry of the reaction in two ways. First, stabilization of the betaine by solvation decreases the rate of dissociation of the betaine to starting material thus inhibiting the thermodynamic control of the reaction. Second, the relative stabilities of the betainescan be altered by the nature of the reaction conditions. In aprotic solvents, the betaine will be most stable in the synperiplanar conformations, VIII, IX, where the oppositely charged phosphorus and oxygen atoms are at a minimum distance. This means that VIII is more stable than IX, since the bulky substituents are not eclipsed. This results in a preference for the trans olefin. Coordination of Lewis acids with the oxygen of the betaine reduces the electrostatic attraction

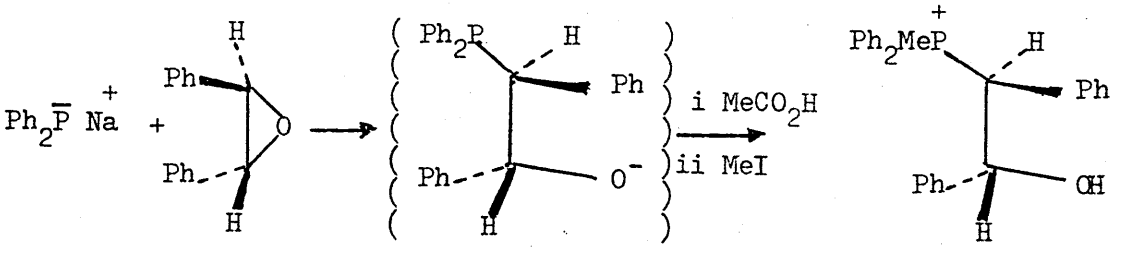
between phosphorus and oxygen atoms. Thus the antiperiplanar conformations X, XI, become more stable. Of these two forms XI will be favoured since it has the less sterically crowded arrangement of the substituents. This results in an increased proportion of the cis olefin being formed. This explanation is illustrated in Scheme 5.

Scheme 5.

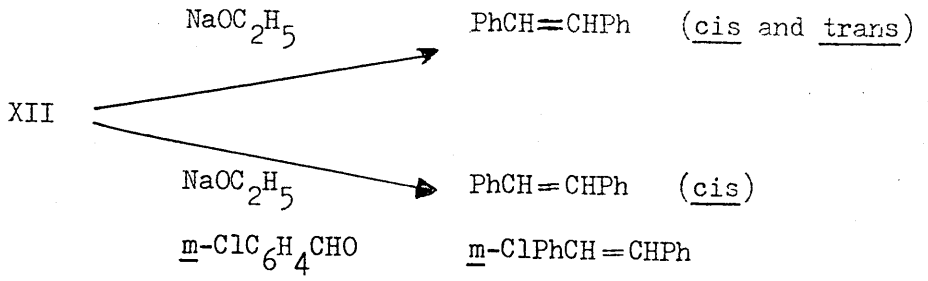


Wittig reactions involving semi-stabilized ylids have also been studied. Trippett[37] prepared diastereomerically pure β-hydroxyphosphonium iodide XII from trans stilbene oxide and sodium diphenylphosphine followed by protonation with glacial acetic acid and quarternisation with methyl iodide, Scheme 6. Deprotonation of the β-hydroxyphosphonium salt by sodium ethoxide generated an erthyro betaine. Depending upon the degree of reversibility this can decompose to give the cis olefin or dissociate to give the ylid and aldehyde which recombine to give a mixture of erythro and threo betaines. An observed cis:trans ratio of 60:40 was obtained indicating some reversibility. When this reaction was carried out in the presence of the more reactive m-chlorobenzaldehyde, cis stilbene and m-chlorostilbenes were produced in the ratio 2:3. This indicates that the betaine dissociates to reactants faster than it decomposes to products. Absence of trans stilbene in the products, ruled out the epimerisation of the betaines, all of the ylid formed by dissociation of erythro betaine, being trapped by the more reactive m-chlorobenzaldehyde.

Scheme 6.



XII



Bergelson[41] studied the effect of solvent and of added lithium salts on the stereochemistry of the products formed in the reaction between benzylidenetriphenylphosphorane and propionaldehyde or benzaldehyde. In general the predominant product was the trans olefin.[42,43] When polar solvents such as dimethylformamide were employed an increased proportion of the cis olefin was produced. A similar effect was observed when lithium halides were added to the reaction mixture. These results are illustrated in Table 6. A similar explanation applies to these results as that proposed in the case of the stabilized ylids.

Table 6. The effect of solvent and lithium halides on the steric course of the reaction of benzylidenetriphenylphosphorane with propionaldehyde and benzaldehyde

Aldehyde used	Solvent	Cis:Trans Ratio			
		Salt-Free	LiCl	LiBr	LiI
C_2H_5CHO	DMF	41:59	39:61	41:59	44:56
C_6H_5CHO	DMF	-	60:40	62:38	63:37
C_2H_5CHO	Benzene	18:82	21:79	27:73	41:59
C_6H_5CHO	Benzene	34:66	38:62	50:50	45:55
C_2H_5CHO	Hexane	22:78	23:77	-	31:69
C_2H_5CHO	Ether	23:77	21:79	-	33:67

Similar experiments were performed to investigate the reaction of non-stabilized ylids with aldehydes. Speziale and Bissing[36] studied the reaction of 4-octene oxide with tributyl or triphenylphosphine in the presence of m-chlorobenzaldehyde. They found that the m-chlorobenzaldehyde was incorporated into the product olefin, demonstrating that for these non-stabilized ylids the Wittig reaction was also reversible. The results of the reactions of 4-octene oxide and other epoxides are shown in Table 7.

Table 7. Results of Reactions between R_3P and $R^1CH—CHR^2$ (O) in the presence of m-ClC_6H_4CHO.

R	R^1	R^2	Epoxide	A mole %		B mole %	
				Cis	Trans	Cis	Trans
$n\text{-}C_4H_9$	$n\text{-}C_3H_7$	$n\text{-}C_3H_7$	Cis	16.4	40.6	17.2	26.8
$n\text{-}C_4H_9$	$n\text{-}C_3H_7$	$n\text{-}C_3H_7$	Trans	49.1	7.6	15.3	28.0
C_6H_5	$n\text{-}C_3H_7$	$n\text{-}C_3H_7$	Cis	30.5	54.7	6.3	8.5
C_6H_5	$n\text{-}C_3H_7$	$n\text{-}C_3H_7$	Trans	11.8	7.0	8.5	0.2
C_6H_5	C_6H_5	C_6H_5	Cis	22.8	12.0	43.8	1.3
C_6H_5	C_6H_5	C_6H_5	Trans	22.3	22.3	16.0	39.4
C_6H_5	CO_2Et	C_6H_5	Cis	2.1	37.8	3.6	40.7
C_6H_5	CO_2Et	C_6H_5	Trans	8.9	6.8	4.3	62.1

A : $R^1CH=CHR^2$

B : m-$ClC_6H_4CH=CHR^1$

These results indicate that the degree of reversibility as demonstrated by the incorporation of m-chlorobenzaldehyde in the products, increases with the stability of the corresponding ylid. This is because, the more stable the ylid, the more likely it will be that the betaine will dissociate to give the reactants. They also show that the betaine produced by tributylphosphorane is more likely to revert to reactants than that produced by triphenylphosphine. This suggests that an increase in the electron density on the phosphorus atom retards the betaine ring closure which leads to olefin formation.

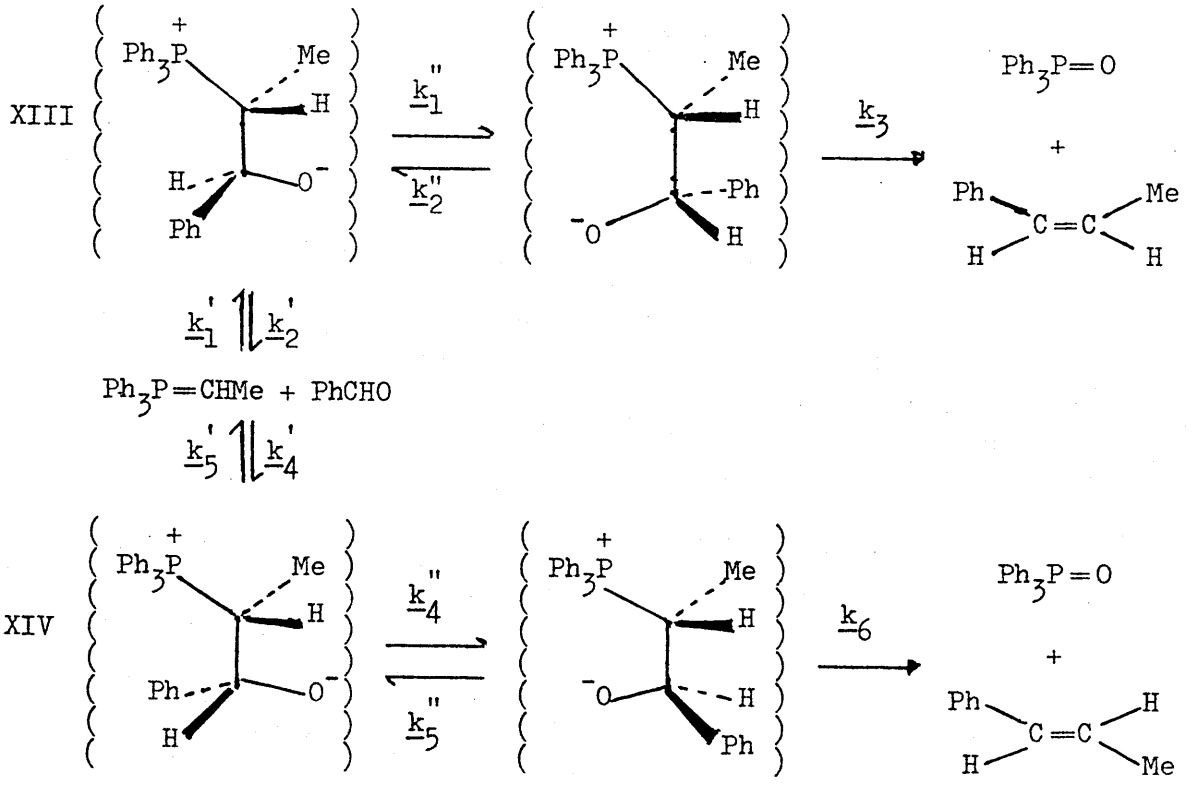
An extensive study of the effect of solvent and added lithium salts on the reactions of non-stabilized ylids such as ethylidene-triphenylphosphorane with propionaldehyde and benzaldehyde, has also been performed.[44–46] This study showed that cis olefins were favoured in both polar and non-polar solvents in the absence of lithium halides but only in polar solvents in the presence of lithium halides. The proportion of trans olefin increased when reaction was carried out in a non-polar solvent in the presence of lithium halides. The results are shown in Table 8.[41]

Table 8. The effect of solvent and lithium halide on the steric course of reaction of ethylidenetriphenylphosphorane with propionaldehyde and benzaldehyde

Aldehyde used	Solvent	Cis:Trans Ratio			
		Salt-Free	LiCl	LiBr	LiI
		A	B	C	D
C_2H_5CHO	DMF	93:7	94:6	94:6	95:5
C_6H_5CHO	DMF	79:21	73:27	71:29	74:26
C_2H_5CHO	Benzene	92:8	89:11	90:10	77:23
C_6H_5CHO	Benzene	91:9	79:21	60:40	35:65
C_6H_5CHO	Hexane	89:11	83:17	79:21	61:39
C_6H_5CHO	Ether	92:8	80:20	37:63	22:78

To explain these results we need to consider the relative sizes of the rate constants in Scheme 4 for the formation of cis and trans olefins. From Scheme 4, it would be expected that k_2 is greater than k_5 because k_2 represents the dissociation of the more sterically crowded intermediate VI to phosphorus ylid and carbonyl compounds. k_3 would also be expected to be less than k_6 since k_6 represents the formation of the thermodynamically more stable trans olefin. According to equation (19), in order to satisfy the experimentally observed cis:trans ratio greater than one, k_1 should be greater than k_4. This however, is very unlikely since k_1 represents the formation of the sterically more crowded intermediate VI and would be expected to be less than k_4. In order to explain this anomaly, Bergelson[47-49] suggested that reactions with unstabilized ylids an 'early' transition state would enable the formation of betaine intermediates XIII or XIV as illustrated in Scheme 7.

Scheme 7.

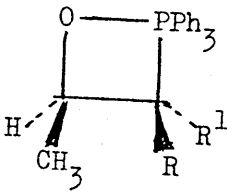


XIII is less sterically unfavourable than XIV and hence would be expected to be more stable. Internal rotation of XIII leads to XV which would collapse to the cis olefin. This means that k_1' is greater than k_4' leading to a predominance of the cis olefin. There is other evidence which supports the idea of an early transition state. Bergelson[50] observed that the ρ value for the reactions of unstabilized ylids with various substituted aldehydes is +1.0 whereas with stabilized and semi-stabilized ylids the ρ value is above +2.7. The positive value indicates that betaine formation is still relatively slow with respect to decomposition to product olefin and phosphine oxide. However the lower value implies a reduced sensitivity to substituent effects. This is consistent with a low degree of bond formation and charge separation in the transition state. The effect of adding various lithium halides to the reactions between non-stabilized ylids and carbonyl compounds has been studied. The reaction times increased in the order LiCl < LiBr < LiI.[41] This is probably the result of complexation with the betaine promoting its equilibration to reactants. This favours the production of the more thermodynamically favoured trans product.

Other mechanisms have been proposed to explain the predominance of cis olefin as the result of reactions between non-stabilized ylids and carbonyl compounds. Vedejs and Snoble[51,52] carried out low temperature ^{31}P n.m.r. studies of the reaction between ethylidenetriphenylphosphorane and various carbonyl compounds. They found that the phosphorus ylid and carbonyl compounds reacted to give the oxaphosphetane directly and they could not detect any trace of the betaine. This result indicated that the oxaphosphetane had a lower energy than was previously thought. The results obtained are given in Table 9.

Table 9. Oxaphosphetanes from the Wittig reaction of Ethylidenetriphenylphosphorane in THF[51].

Carbonyl component	Oxaphosphetane	Cis:Trans olefin ratio
Cyclohexanone	1a,b	99:1
$(CH_3)CCHO$	2a,b	2:1
C_6H_5CHO	3a,b	7:3
$C_6H_5CH_2CH_2CHO$		



1a, R = $C(CH_3)_3$; R^1 = H

1b, R = H; R^1 = $C(CH_3)_3$

2a, R = C_6H_5; R^1 = H

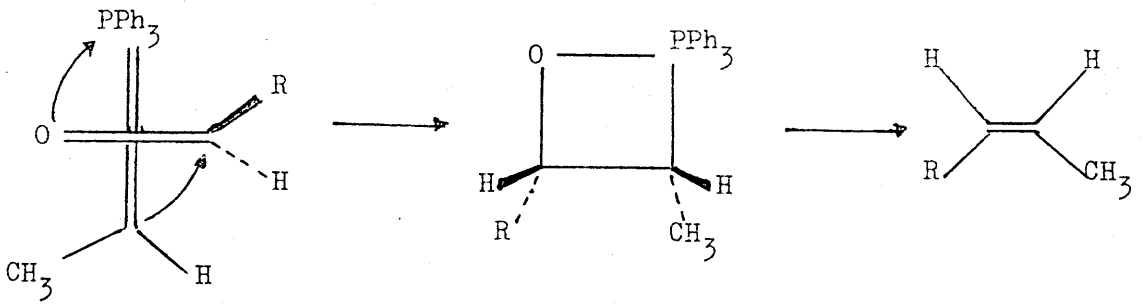
b, R = H; R^1 = C_6H_5

3a, R = $C_6H_5CH_2CH_2$; R^1 = H

b, R = H; R^1 = $C_6H_5CH_2CH_2$

The mechanism suggested for oxaphosphetane formation was a $\pi^2_s + \pi^2_a$ cycloaddition. The orthogonal approach of ylid and aldehyde double bonds in the least hindered arrangement would lead to the most hindered oxaphosphetane and hence the cis olefin after elimination of triphenylphosphine oxide as shown in Scheme 8.

Scheme 8.



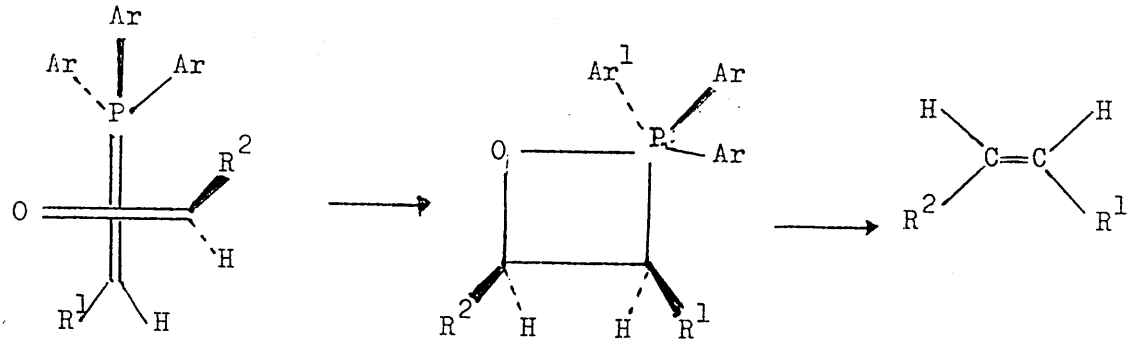
Further support for the cycloaddition mechanism comes from the work of Allen et al. They studied the effect of steric crowding at the phosphorus by reacting a series of semi-stabilized triarylphosphonium ylids in ethanol.[53,54] The results are given in Table 10. Tris-o-tolylphosphonium ylids give rise to a higher cis:trans ratio than the corresponding trisphenylphosphonium ylids. This was due to a steric effect and not an electronic effect since the result obtained using tris-p-tolylphosphonium ylids was similar to that obtained using triphenylphosphonium ylids. The results were found to be independent of whether lithium ethoxide or sodium ethoxide were used to generate the ylid.

Table 10. Cis:Trans Ratios and Total Yields of Stilbenes from the Reaction of the Ylids $Ar_2^1Ar^2P{=}CHPh$ with benzaldehyde

Ylid	cis:trans ratio (%)	Total yield of stilbenes (%)
(a) $Ar^1 = Ar^2 =$ Ph	40:60	60
(b) $Ar^1 =$ Ph; $Ar^2 =$ o-tolyl	62:38	69
(c) $Ar^1 =$ o-tolyl; $Ar^2 =$ Ph	67:33	>95
(d) $Ar^1 = Ar^2 =$ o-tolyl	70:30	76
(c) $Ar^1 = Ar^2 =$ p-tolyl	42:58	>95

They proposed that the increase in steric crowding at phosphorus favoured the transition state XVI in which the group R^2 is directed away from the bulky phosphorus leading to the erythro 1,2-oxaphosphetane and hence the cis olefin.

Scheme 9.



XVI

When the reaction was repeated in an aprotic solvent such as tetrahydrofuran[54] using butyllithium to generate the phosphorus ylid, a different set of results were obtained as shown in Table 11.

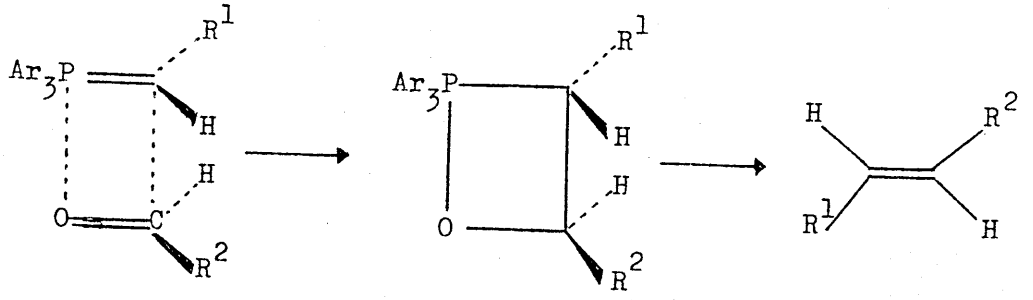
Table 11 Cis:trans Ratios of stilbenes formed in Wittig reactions of semi-stabilized ylids $Ar_2^1 Ar^2 P{=}CHPh$ with benzaldehyde in tetrahydrofuran

Ylid	cis:trans ratio (%)	Total Yield (%)
$Ar^1 = Ar^2 = Ph$	60:40	95
$Ar^1 = Ph, Ar^2 =$ o-tolyl	61:39	70
$Ar^1 =$ o-tolyl; $Ar^2 = Ph$	46:54	72
$Ar^1 = Ar^2 =$ o-tolyl	21:79	54
$Ar^1 = Ar^2 =$ p-tolyl	57:43	59

These results were explained by proposing that the betaine intermediate is stabilized by coordination to the lithium ion so that it becomes lower in energy than the oxaphosphetane. Increased steric crowding at phosphorus would be expected to lead to a decrease in the rate of nucleophililic attack at phosphorus and hence in the rate of betaine collapse to products. This enhances the reversibility leading to a preference for the threo betaine on thermodynamic grounds. This results in an increase in the proportion of trans alkene in the presence of lithium ions.

The cycloaddition mechanism can also account for the preference for trans-olefin when stabilized ylids react with carbonyl compounds.[55] In this case it is believed that a coplanar combination of the reactants in a $\pi^2_s + \pi^2_s$ cycloaddition gives the sterically favoured trans oxaphosphetane which on elimination of triphenylphosphine oxide gives the trans olefin as shown in Scheme 10.

Scheme 10.

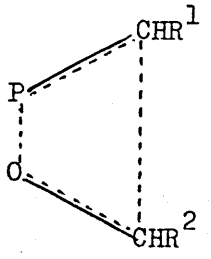


Results supporting this mechanism are given in Table 12.

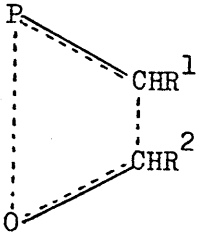
Table 12. The results of Wittig reactions between stabilized ylids $Ar_3P{=}CHCO_2Et$ with the aldehydes RCHO in ethanol.[56]

	RCHO	% cis	% trans	Overall Yield %
Ar=phenyl	R=Ph	21	79	89
Ar=2-furyl	R=Ph	41	59	31
Ar=phenyl	R=Me	27	73	71
Ar=2-furyl	R=Me	48	52	22

The effect of electron withdrawing substituents at phosphorus, such as 2-furyl, was to increase the proportion of the cis isomer. This was explained by proposing that the P·····O bond is formed in advance of the C·····C bond. Therefore steric interactions between the substituents on the ylid carbon and carbonyl carbon are decreased and have less effect on the stability of the transition state XVII. Conversely, in the case of electron donating substituents at phosphorus, such as phenyl, formation of the C·····C bond precedes that of the P·····O. Thus steric interactions between the substituents at the carbon atoms are increased (XVIII) and would therefore favour the trans isomer.



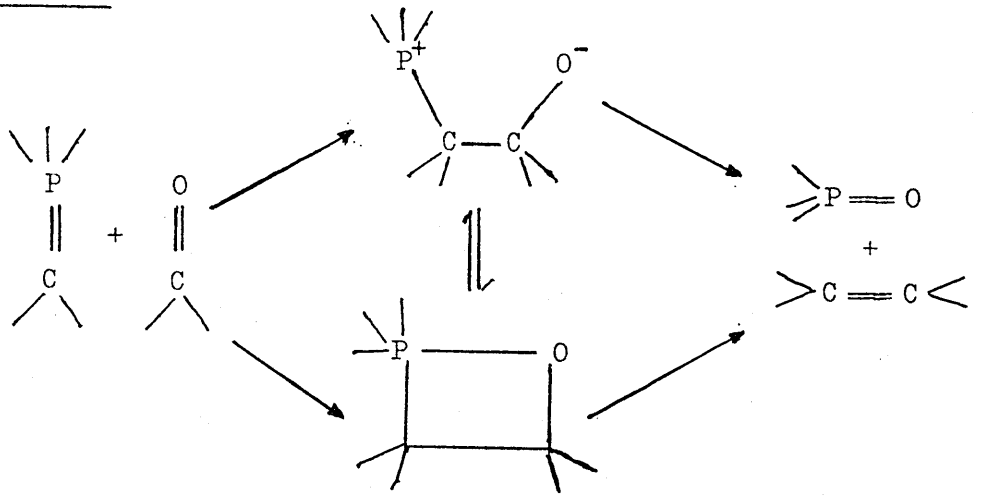
XVII



XVIII

However, the results of Schlosser and Tuong[57] do not agree with the 2+2 cycloaddition mechanism. They contended that this mechanism did not fully account for the cis stereochemistry of the Wittig reaction in salt free media. They proposed that the reaction proceeded via a betaine-like transition state and that an equilibrium is established between the betaine and oxaphosphetane as illustrated in Scheme 11 below.

Scheme 11.

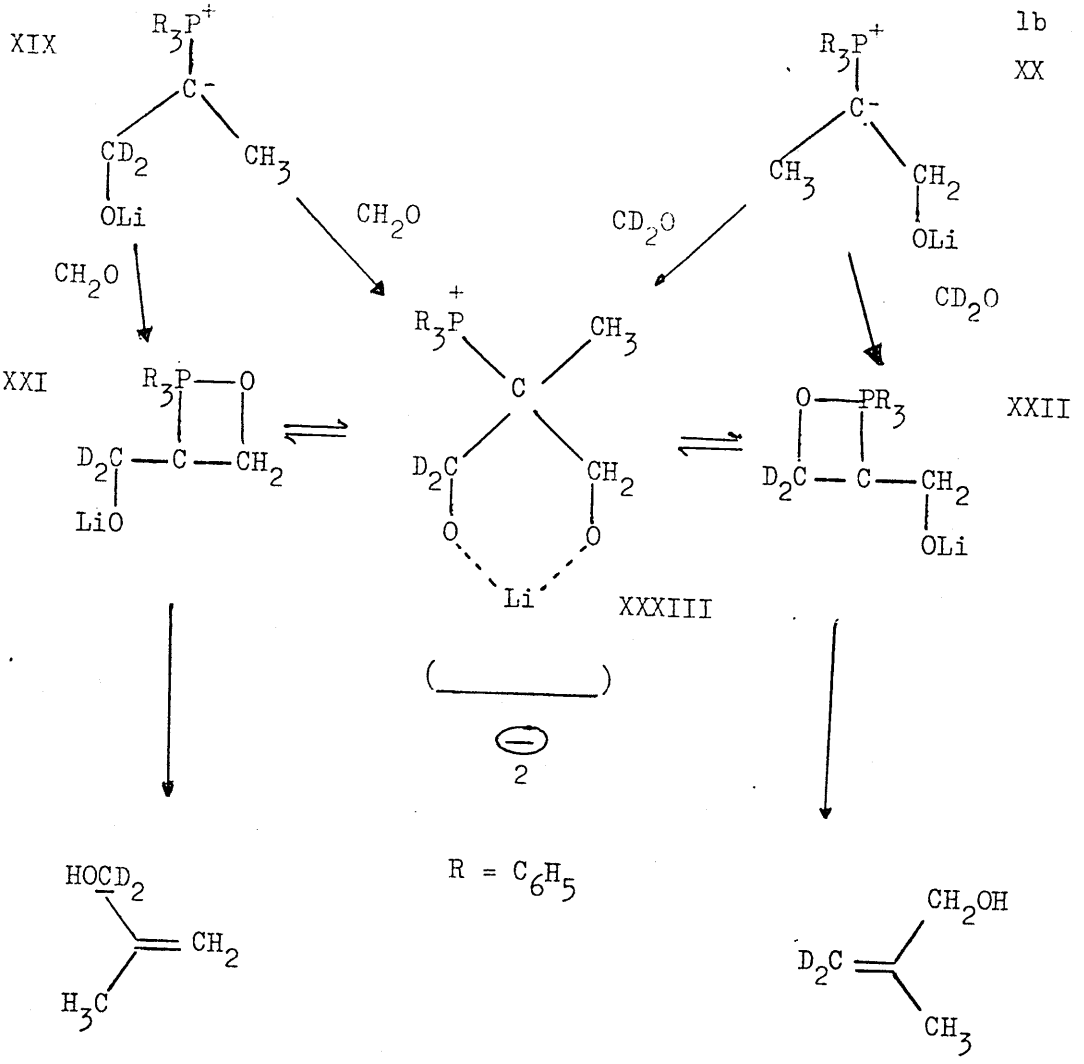


Evidence to support this was obtained by carrying out experiments using isotopically labelled ylids and aldehydes.

A solution of salt free ethylidenetriphenylphosphorane in tetrahydrofuran was treated at -75°C consecutively with formaldehyde solution and sec-butyllithium. Dideuterioformaldehyde was then added to the resulting betaine ylid XX. After subsequent addition of potassium tert-butoxide and warming to 25°C, 2-methylallyl alcohol could be separated in 80% yield. The product was deuteriated equally at the carbon adjacent to oxygen and the terminal olefinic carbon. The same product mixture was obtained when deuterium-free formaldehyde was added to the deuteriated betaine-ylids XIX. These

reactions are illustrated in Scheme 12 below.

Scheme 12.

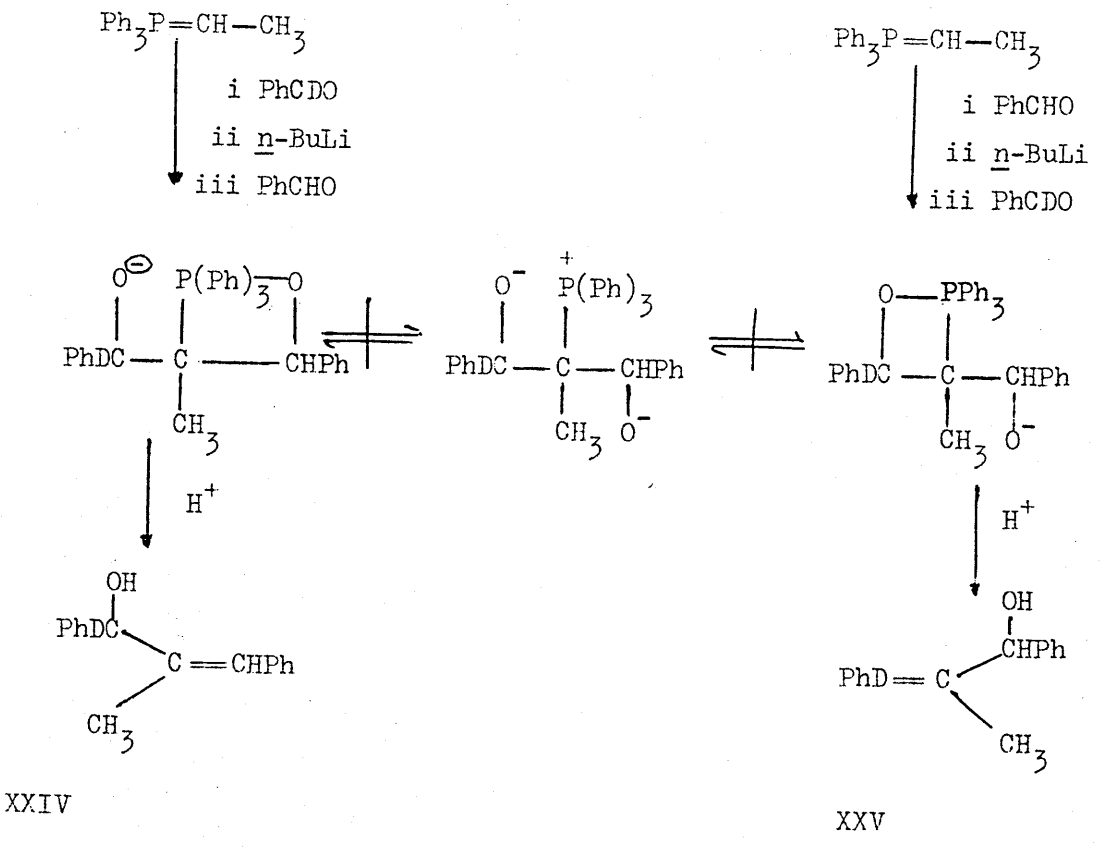


^{31}P n.m.r. studies of the reaction mixture gave spectra which were consistent with the presence of an oxaphosphetane. The formation of equal quantities of deuteriated 2-methylallyl alcohol indicated that an equilibrium must exist between oxaphosphetanes XXI and XXII, presumably via the betaine XXIII. These results, however, do not give any information as to whether the intermediate oxaphosphetanes were formed directly or indirectly via a betaine precursor. In either respect the species XXI, XXII and XXIII must be in

equilibrium with each other at -80°C. This was confirmed by adding acetyl chloride, which reacts spontaneously with lithium alkoxide at -80°C, to the betaine-ylid/formaldehyde adduct 2-methyl-allyl. Once again both types of methylene groups were equally isotopically labelled.

The presence of an equilibrium between the oxaphosphetane and betaine has been questioned by Bestman.[58] He argued that since the allyl alcohols were worked up the presence of potassium tert-butoxide, deuterium exchange could occur between the acidic allylic positions. This would account for the mixture of labelled allyl alcohols produced. The work of Corey[59] also casts doubts on the presence of an equilibrium between oxaphosphetane and betaine. He carried out essentially similar experiments to Schlosser but used benzaldehyde instead of formaldehyde as shown in Scheme 13.

Scheme 13.

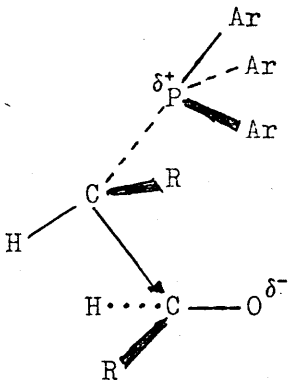


XXIV

XXV

In this case ethylidenetriphenylphosphorane was reacted sequentially with 1-deuteriobenzaldehyde, n-butyllithium and unlabelled benzaldehyde. This gave XXIV as the exclusive product. Similarly, the treatment of ethylidenetriphenylphosphorane sequentially with unlabelled benzaldehyde, n-butyllithium and 1-deuteriobenzaldehyde gave XXV exclusively. From these results it would appear that it was the oxygen of the aldehyde which was added to the reaction mixture last that was eliminated in the triphenylphosphine oxide. The results also indicate that an equilibrium between the possible oxaphosphetanes and betaine does not exist.

A variation on the 2+2 cycloaddition mechanism has been proposed by Bestmann.[58,60,61] He suggested that the ylid and carbonyl compound react to give the cis oxaphosphetane via a betaine-like transition state XXVI.

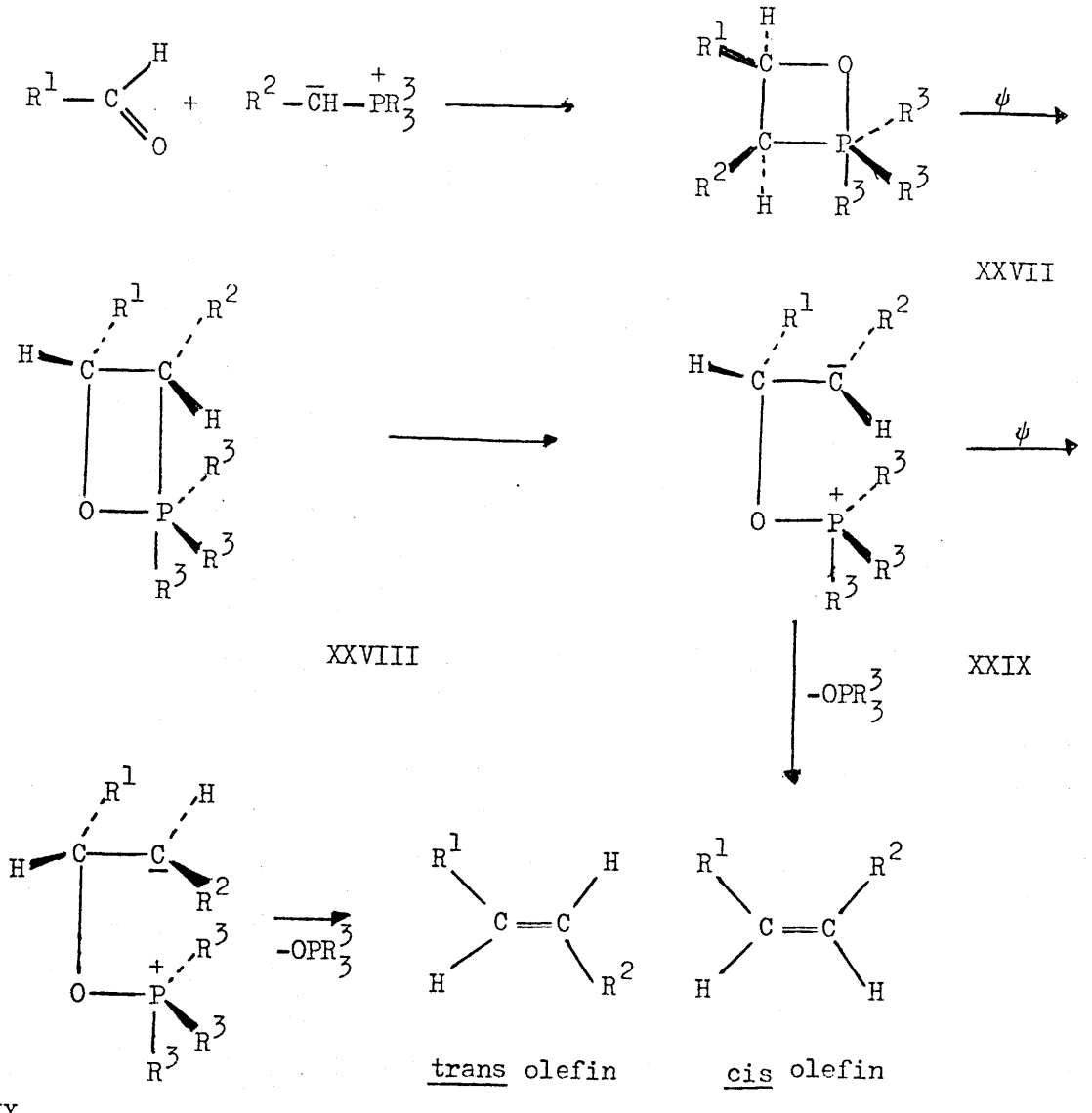


XXVI

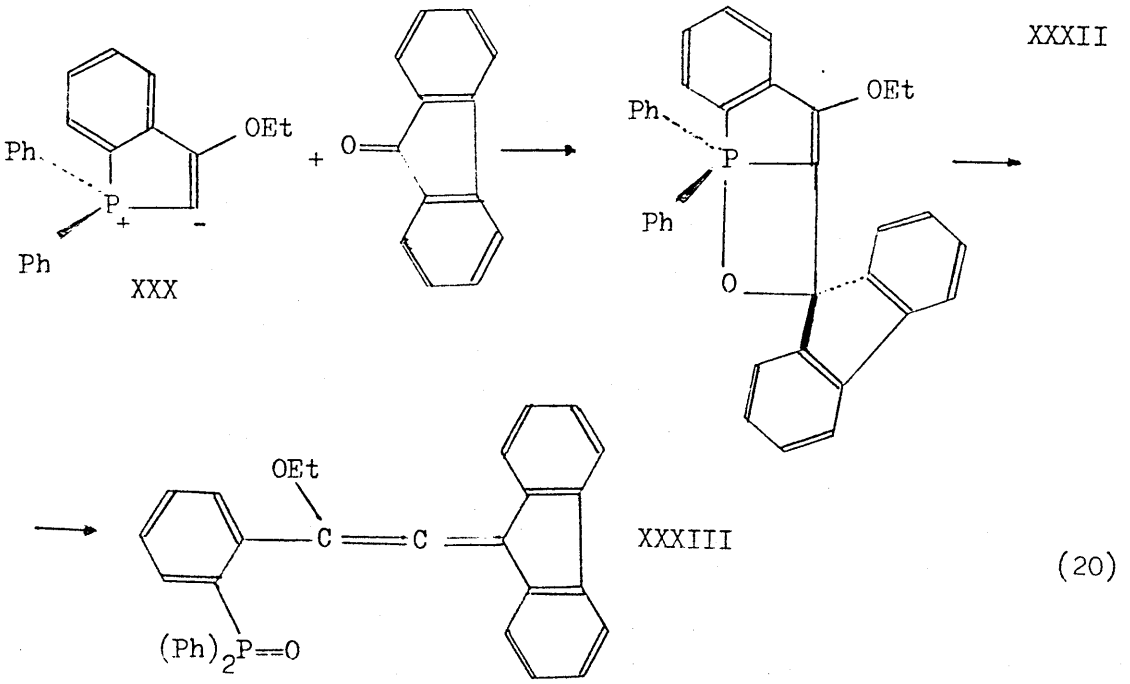
In the cis oxaphosphetane produced XXVII the oxygen occupies an apical position. This undergoes rearrangement of the ligands (pseudorotation) so that the phosphorus carbon bond now occupies the apical position XXVIII. In the course of this rearrangement or after the structure is formed, the carbon phosphorus bond cleaves to give the betaine XXIX. It is at this point that the stereochemistry of the product olefin is determined. If R^2 is an electron donor, such as alkyl, and the ligands R^3 are phenyl groups a very rapid elimination of triphenyl-

phosphine oxide takes place to give cis olefin. If R^2 is an electron acceptor such as an ester group the lifetime of XXIX is increased allowing rotation about the carbon bond to give the thermodynamically more stable conformation XXX from which trans olefin can be formed. Similarly, when the substituents R^3 have donor properties such as alkyl or cyclohexyl groups, the phosphine oxide cleavage is retarded enhancing the probability of the conformational change XXIX⟶XXX. As a result, a sharp decrease in the cis:trans ratio is observed on going from R^3 = phenyl to R^3 = alkyl or cycloalkyl. The mechanism is illustrated in Scheme 14.

Scheme 14.



Evidence in support of this mechanism was provided by Bestmann.[58,62] The reaction of XXX with flurorenone gave a crystalline adduct XXXII. X-ray analysis proved that the oxygen occupies an apical position relative to the phosphorus. The adduct decomposes on boiling in toluene or upon heating above its melting point to give a mixture of the starting compounds and the allene XXXIII. This is illustrated in equation 20.



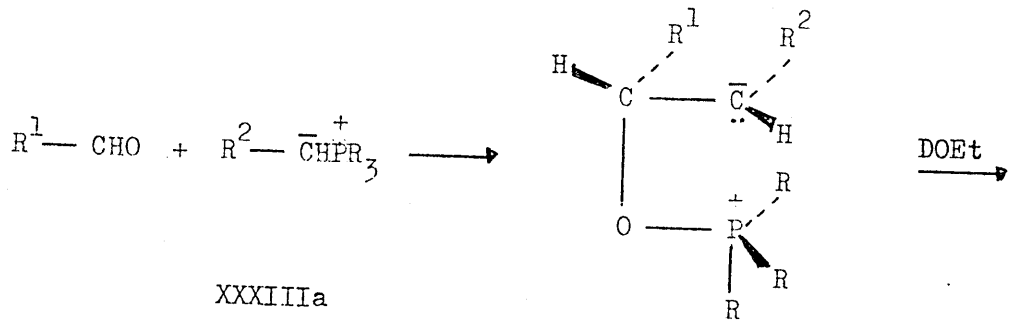
(20)

It is argued that this supports the proposed ligand reorganisation (pseudorotation) because the allene was only formed on heating, indicating that some sort of rearrangement had to occur before the reaction was possible.

Bestmann[58] also provided evidence for the initial phosphorus carbon bond cleavage XXVIII ⟶ XXIX. When an aldehyde was mixed with XXXIIIa at -78°C followed by addition of ethanol, an increase in the formation of the trans olefin was observed. If deuterated ethanol was used deuterium was incorporated into the product olefin, considerably more being incorporated in the trans isomer than the cis isomer.

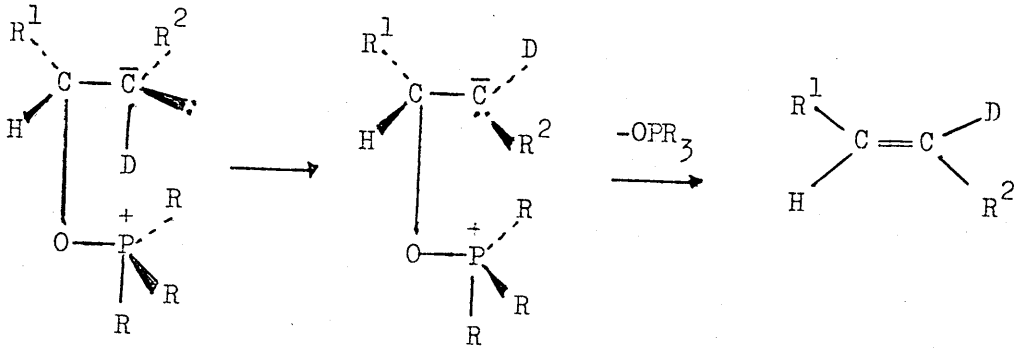
Based on this investigation the following reaction mechanism was proposed (Scheme 15).

Scheme 15.



XXXIIIa

XXXIV



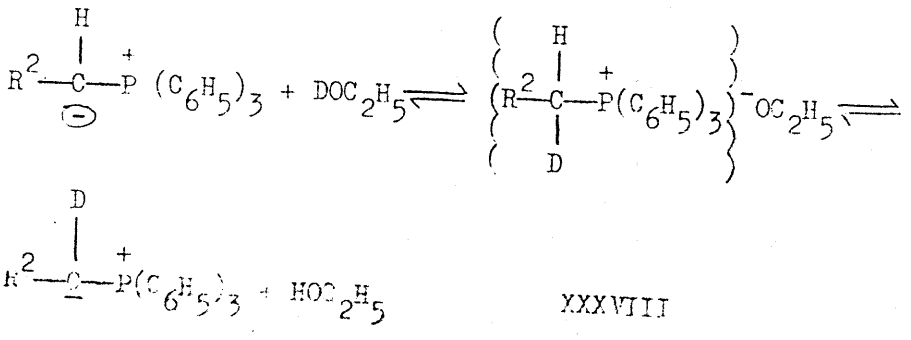
XXXV

XXXVI

XXXVII

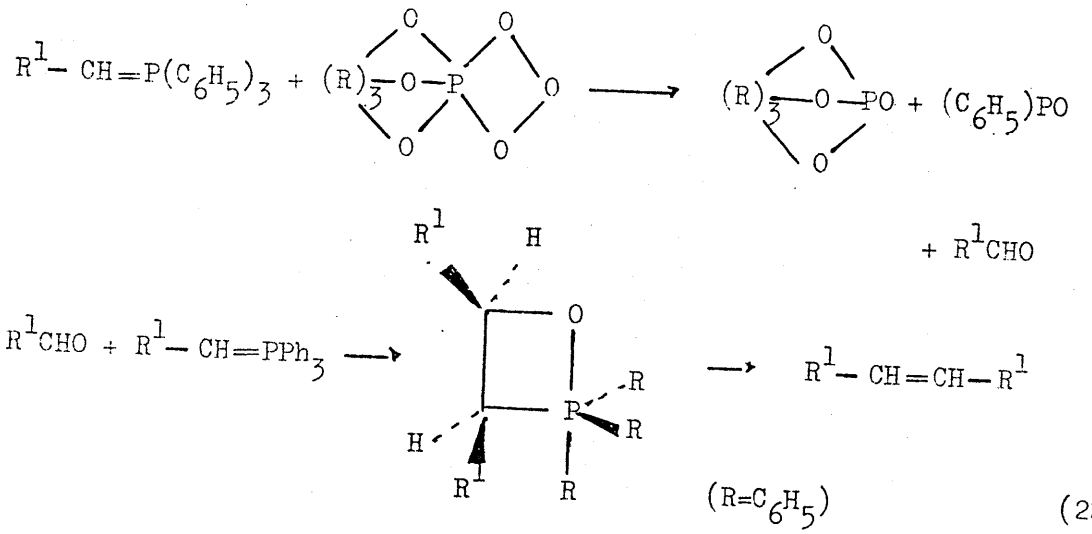
The betaine XXXIV reacts with the alcohol to give XXXV via synchronous addition and elimination of a deuteron and a proton respectively. The betaine XXXV then converts to XXXVI, which upon elimination of phosphine oxide yields the trans isomer with incorporation of the deuterium.

In principle the incorporation of deuterium in the product may also be explained by proposing an equilibration between the phosphorus ylid and its deuteriated form XXXVIII.[63] However, the preferential incorporation of deuterium into the trans olefin argues against this possibility.



XXXVIII (21)

Evidence against the equilibrium given in equation 21, is also provided by treating alkylidenetriphenylphosphorane with phosphite-ozone adducts to give olefins[64] by the series of reactions illustrated in equation 22.

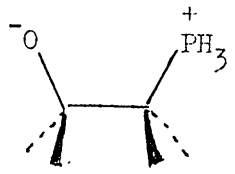


(R=C_6H_5) (22)

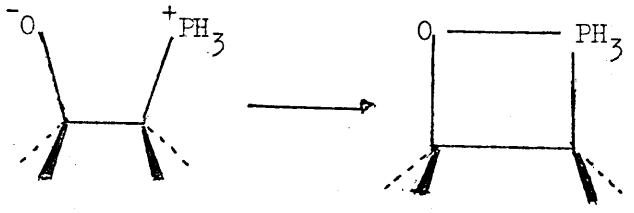
When this reaction was carried out in the presence of deuterated ethanol at -78°C the resulting olefin contained only one deuterium atom. If there was an equilibrium between the phosphorus ylid and its deuterated form XXXVIII, then olefins with 2 deuterium atoms would be formed. This indicates that inclusion of the deuterium occurs only after initial cleavage of the phosphorus carbon bond in the oxaphosphetane.

Further evidence for the initial phosphorus carbon bond cleavage comes from CNDO-MO calculations.[65] The four possible mechanisms for olefin formation are given below for a model.

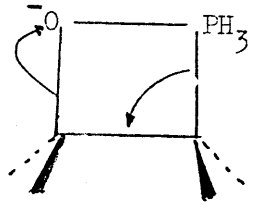
1. Concerted decomposition of betaine.



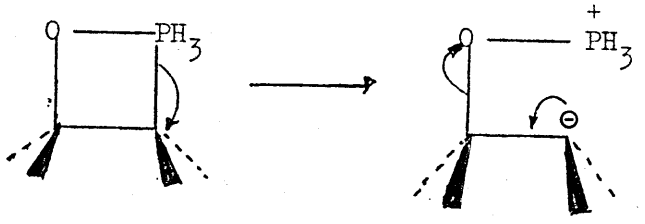
2. Initial formation of a dihydrooxaphosphetane followed by three possible modes of decomposition.



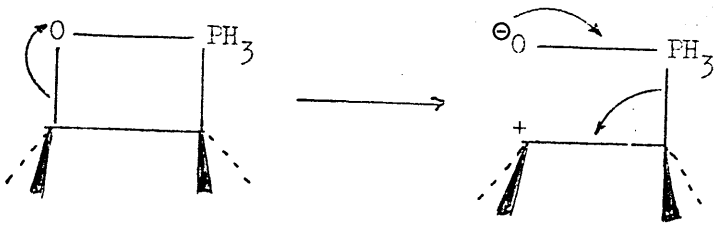
2a. Concerted decomposition of dihydrooxaphosphetane.



2b. Non-concerted decomposition of dihydrooxaphosphetane involving initial phosphorus carbon bond cleavage.



2c. Non-concerted decomposition of dihydrooxaphosphetane, with initial carbon oxygen bond cleavage.



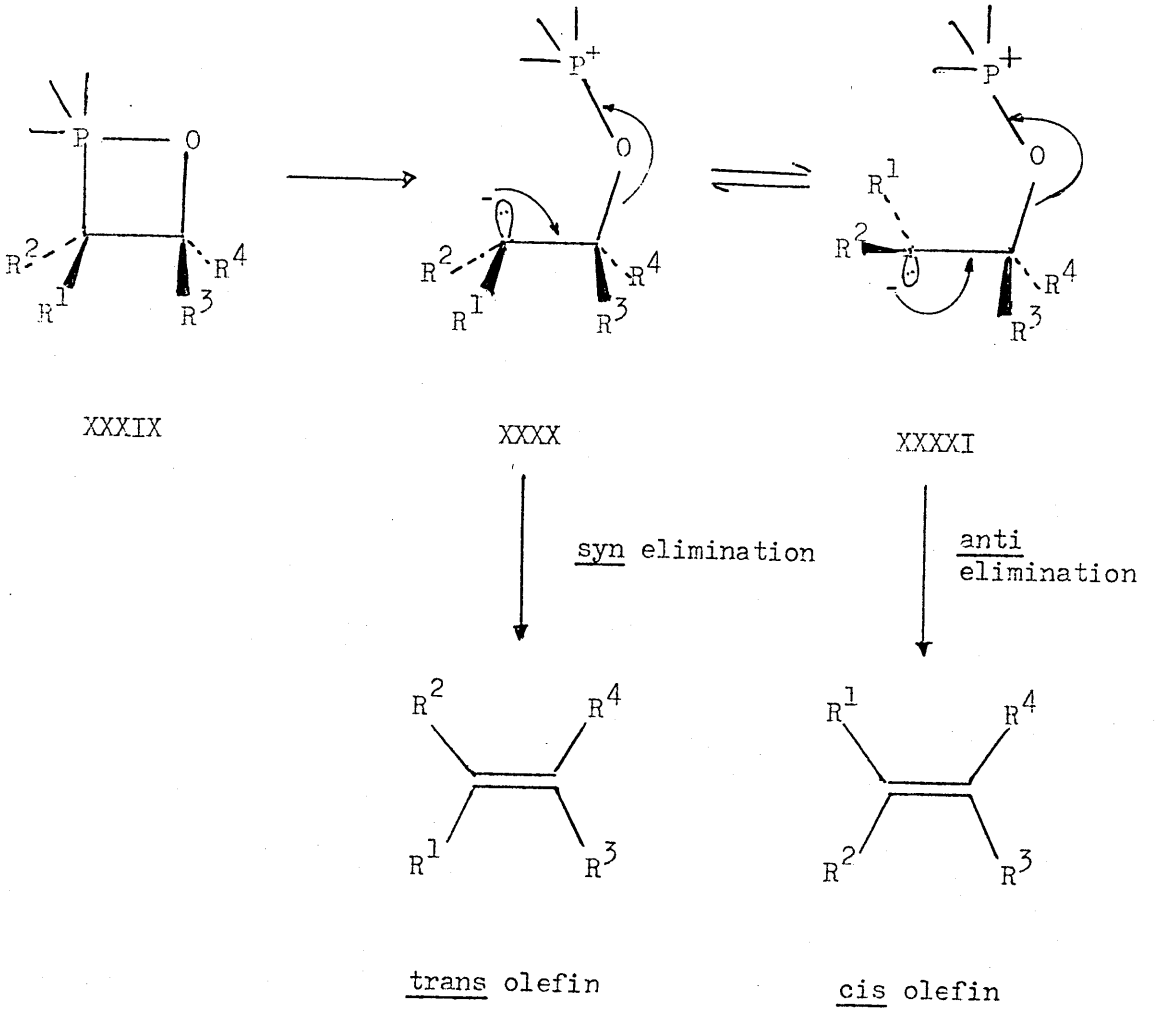
The calculation indicated that the best general description for the decomposition of the betaine intermediate involves an initial reversible formation of a dihydrooxaphosphetane which in turn undergoes fragmentation to olefin and phosphine oxide by a process in which cleavage of the phosphorus carbon bond is considerably advanced over cleavage of the carbon oxygen bond.

A further mechanism has been proposed by Whangbo[66] to explain the formation of cis olefins when non-stabilized ylids react with carbonyl compounds. He proposed that the thermodynamically more stable trans oxaphosphetane would be formed. This was believed to occur because non-stabilized ylids exhibit significant localised carbanion character at the carbon atom.[67—69] Hence the Wittig reaction would involve a typical nucleophilic attack on the carbonyl carbon. By consideration of charge separation and steric hindrance the trans oxaphosphetane is predicted to be the more likely product,[70] as predicted in Scheme 4 with $\underline{k}_1 > \underline{k}_4$. If the oxaphosphetane formation is reversible however, then the trans oxaphosphetane will still predominate because it is the thermodynamically more stable product. To account for trans oxaphosphetane formation but cis olefin products Whangbo proposed the following mechanism.

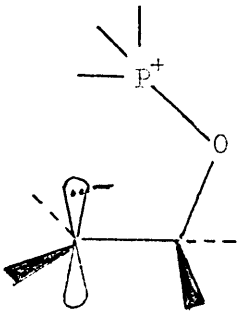
The decomposition of the trans oxaphosphetane XXXIX is again believed to be a non-concerted process in which the cleavage of the

phosphorus carbon bond is well advanced in comparison with that of the carbon oxygen bond. This leads to the intermediate XXXX and its rotamer XXXXI as illustrated in Scheme 16. Whangbo proposed that these intermediates undergo syn elimination in the presence of salts, such as lithium iodide to give trans olefins and anti elimination in the absence of salts to give cis olefins. This behaviour is similar to that observed in Elcb eliminations[71] where syn elimination is favoured in the presence of salts, but anti elimination in the absence of salts.

Scheme 16.



In the case of strongly stabilized ylids the carbanion formed by phosphorus carbon cleavage would be planar[66], XXXXII, because of conjugation with stabilizing substituents. This is followed by elimination of phosphine oxide without rotation about the carbon-carbon bond to give the trans olefin.



XXXXII

1.4 The Peterson Reaction

The Peterson reaction is a method of carbonyl olefination in which an α-silyl carbanion reacts with an aldehyde or ketone to give an alkene as illustrated in equation 21.

$$M^+ R_1R_2\bar{C}SiMe_3 + R_3R_4C{=}O \longrightarrow \begin{pmatrix} R_1R_2C{-}SiMe_3 \\ | \\ R_4R_3C{-}O^- \end{pmatrix} \longrightarrow \begin{matrix} R_1R_2C{=}CR_3R_4 \\ + \\ Me_3Si{-}O^- \end{matrix} \qquad (21)$$

The α-silyl carbanion is believed to be partially stabilized[72,73] by the empty d-orbitals of the silicon atom. This stabilization is not as great as in the case of the phosphorus ylid.[74] In the α-silyl carbanion there appears to be no silicon carbon double bond character and the silicon carries no formal positive charge as does the phosphorus in a Wittig reagent. This positive charge is carried by the metal counterion, usually lithium or magnesium.

The other product of the Peterson reaction is the silanolate anion which is water soluble and easily removed. This is deemed to be an advantage over the Wittig reaction which gives an insoluble side product of phosphine oxide.

1.5 The Nature of the Peterson Reaction

The α-silyl carbanion can be generated from silanes using strong bases such as lithium diisopropylamide (LDA) or butyllithium with hexamethylphosphoramide or tetramethylethylenediamine (TMEDA). These carbanions are very reactive with water and oxygen and must be prepared using anhydrous conditions under an inert atmosphere. Some examples are given in equations 22-24.

$$PhCH_2SiMe_3 \xrightarrow[\text{TMEDA or HMPA}]{\text{n-BuLi}} Ph\bar{C}HSiMe_3\ Li^+ \quad 85\% \qquad (22)^{75,76}$$

$$Me_3SiCH_2CO_2Et \xrightarrow[-78^\circ C]{\text{LDA}} Me_3Si\bar{C}HCO_2Et\ Li^+ \quad > 95\% \qquad (23)^{77}$$

$$Me_3SiCH_2CN \xrightarrow[-78^\circ C]{\text{LDA}} Me_3Si\bar{C}HCN\ Li^+ \quad 90\% \qquad (24)^{78}$$

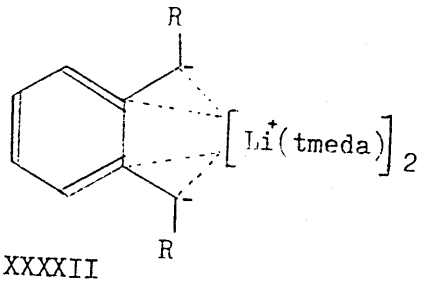
Other methods used to generate α-silyl carbanions are illustrated in equations 25 and 26. The driving force for the reaction shown in equation 25,

$$(Me_3Si)_3CH \xrightarrow[\text{HMPA}]{\text{NaOMe}} (Me_3Si)_2\bar{C}H\ Na^+ + MeOSiMe_3 \quad 82\% \qquad (25)^{79}$$

$$Ph_3SiCH{=}CH_2 \xrightarrow{\text{RLi}} PH_3Si\bar{C}HCH_2R\ Li^+ \quad 77\% \qquad (26)^{80}$$

is the formation of the thermodynamically favoured oxygen silicon bond resulting from the cleavage of the weaker silicon carbon bond.

An X-ray crystal structure of XXXXII has been determined by Lappert.[81] The carbon atoms carrying the negative charge were found to be planar.

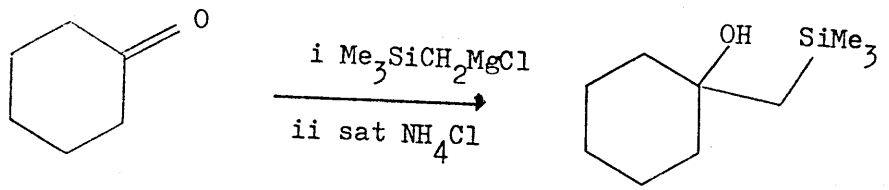


R = $SiMe_3$

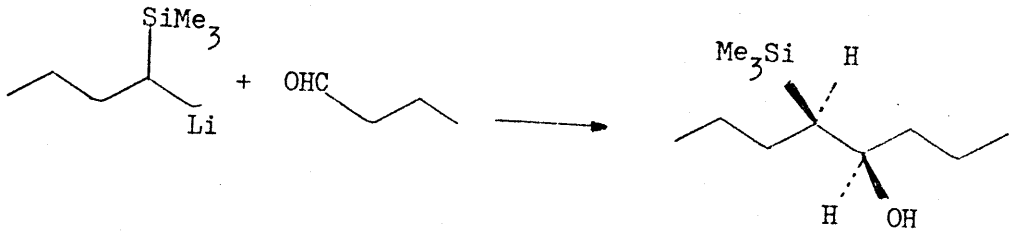
XXXXII

This was believed to be indicative of the aromatic ring stabilizing the negative charge on the adjacent carbon atoms.

When the Peterson reaction is performed with lithium as the counterion and the α-silyl carbanion is stabilized by electron withdrawing groups, such as ester,[77] cyano[78] or phenyl,[75] the reaction proceeds straight to the olefin product,[82] as illustrated in equation 21. If the counterion is magnesium or if the carbanion is not stabilized, the intermediate β-hydroxysilane can often be isolated, as illustrated in equations 27 and 28.



(27)[75]



(28)[83]

It was found that subsequent treatment of the β-hydroxysilane with acid or base yielded the appropriate olefin. The mechanism of formation of the product olefin is dealt with in Section 1.7.

The elimination steps of the Peterson reaction and the Horner Emmons reaction have been compared by carrying out the reaction given in equation 29 and examining the product obtained

$$Me_3Si\bar{C}HP(O)(OEt)_2\ Li^+ + Ph_2C{=}O \longrightarrow Ph_2C{=}CHP(O)(OEt)_2 \qquad (29)^{84}$$

XXXXIII

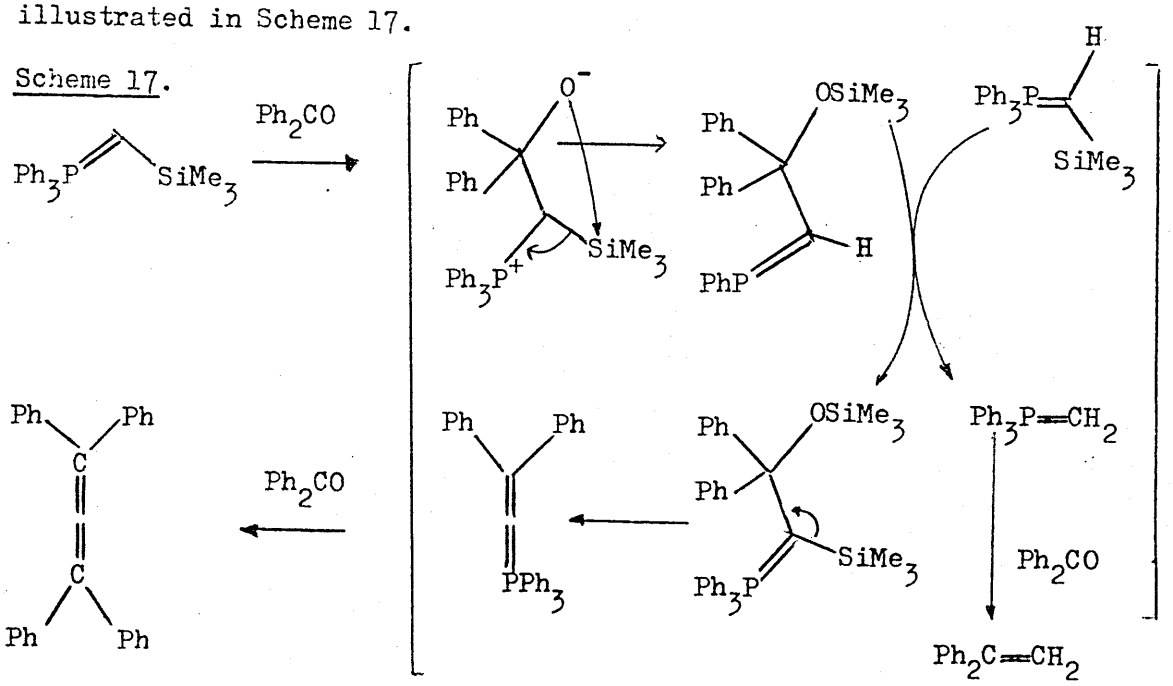
The compound XXXXIII can either undergo a Wittig Horner reaction to give a vinyl silane or a Peterson reaction to give a vinyl phosphate. The formation of the vinyl phosphate indicates that elimination of silanolate is faster than the elimination of phosphate.

Similarly, Gilman and Tomasi[85] compared the Wittig and Peterson reactions. When trimethylsilylmethylenetriphenylphosphorane was reacted with benzophenone, tetraphenylallene and 1,1-diphenylethene were obtained (30).

$$Ph_3P{=}CHSiMe_3 + Ph_2CO \longrightarrow Ph_2C{=}C{=}CPh_2 + Ph_2C{=}CH_2 \qquad (30)^{85}$$

The formation of these products has been explained by Fleming[86] as illustrated in Scheme 17.

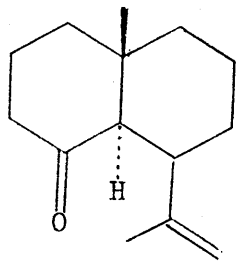
Scheme 17.



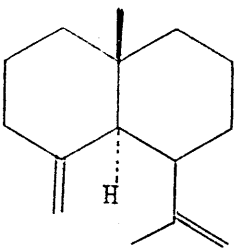
From Scheme 17, it is apparent that the silicon group migrates to oxygen in preference to the phosphorus group. Prior to elimination of silanolate, a silicon group becomes attached to the intermediate enabling the formation of tetraphenylallene by reaction with a further molecule of benzophenone. From this scheme it is apparent that the second step of the Peterson reaction is more favoured than that of the Wittig reaction.

1.6 Applications of the Peterson Reaction

In recent years the Peterson reaction has become important in the synthesis of natural products. The Peterson reaction has often been used as a method of carbonyl olefination when the Wittig reaction has been unsuitable. An example of this is the synthesis of β-gorgonene[87] as illustrated in equation 31.

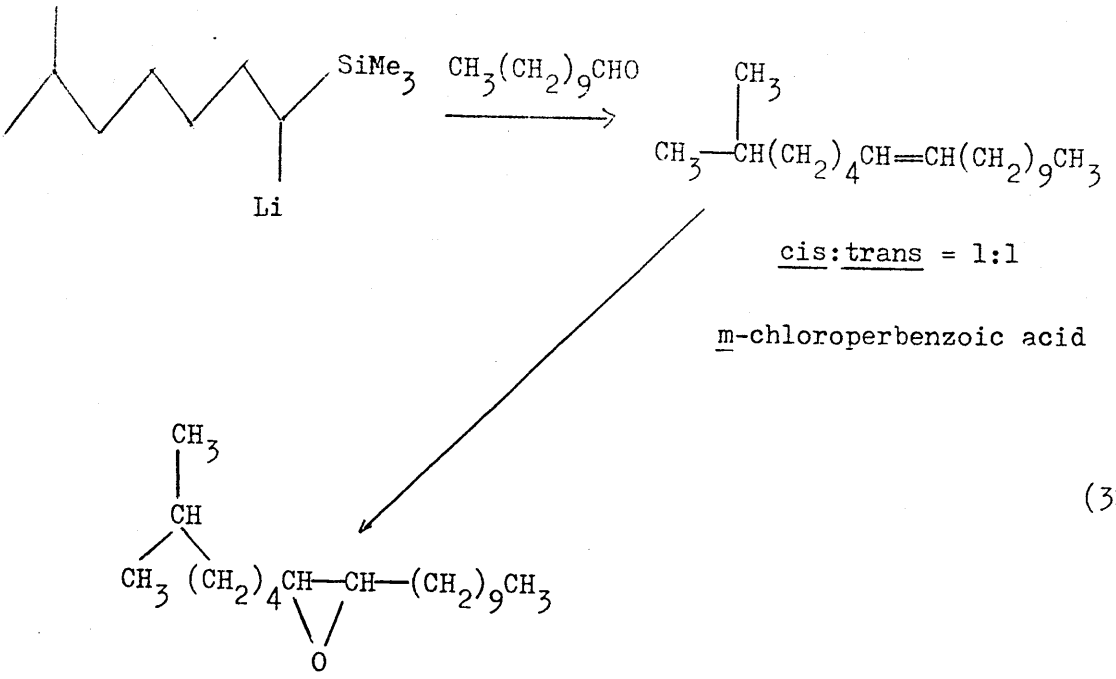


i Me_3SiCH_2MgCl
THF, reflux, 18h
ii AcOH, H_2O, r.t., 3h



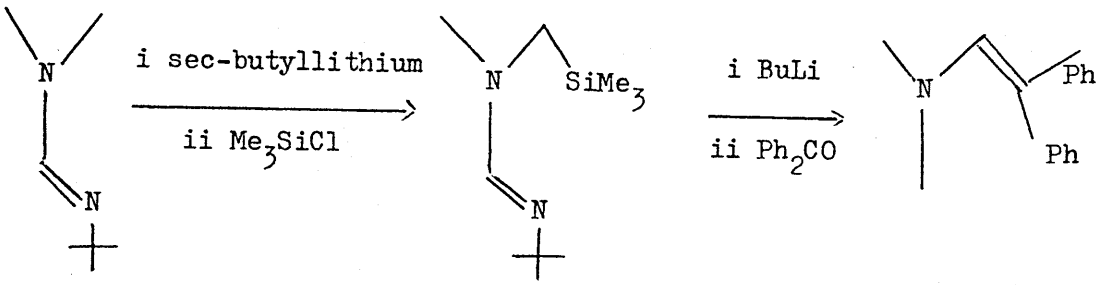
(31)[87]

The Peterson reaction has also been used in the synthesis of the sex pheremone of the gypsy moth[88] as illustrated in equation 32.

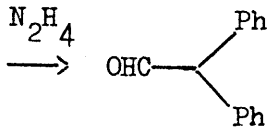


(32)[88]

Recently it has been found that enamidines are very useful reagents for carbonyl homologation,[89] the Peterson reaction being used to generate the enamidine.[90]



(34)



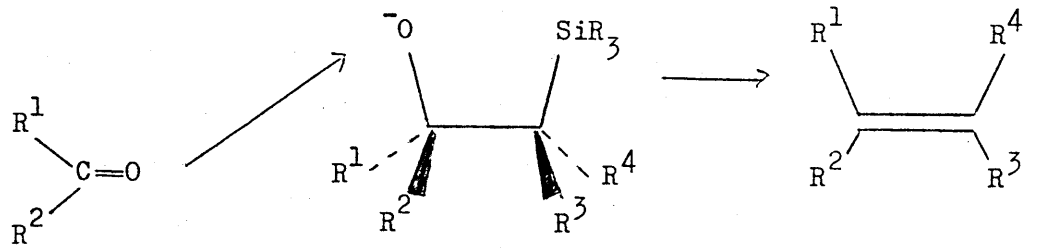
1.7 Stereochemistry and Mechanism of the Peterson Reaction

Whilst the Peterson reaction and Wittig reaction are both methods of carbonyl olefination it is possible that they proceed via different mechanisms. For example, it is very unlikely that a 2+2 cycloaddition mechanism can be invoked for the Peterson reaction as there is no carbon silicon double bond character. This is in contrast with the Wittig reaction where a cycloaddition mechanism is believed to be a distinct possibility.

A mechanism for the Peterson reaction has been proposed by Chan.[91] He believed that the addition of the α-silyl carbanion to the carbonyl compound was irreversible to give equal amounts of the diastereomeric adducts XXXXIV and XXXXV. Each diastereomer eliminates stereospecifically <u>syn</u> to give only one isomer of the alkene as illustrated in Scheme 18.

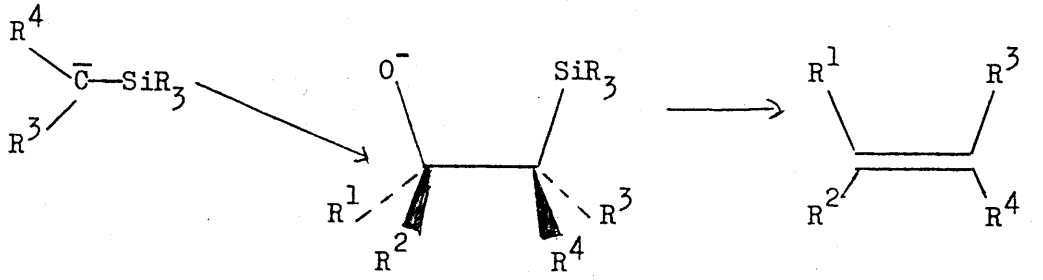
<u>Scheme 18</u>.

XXXXIV



+

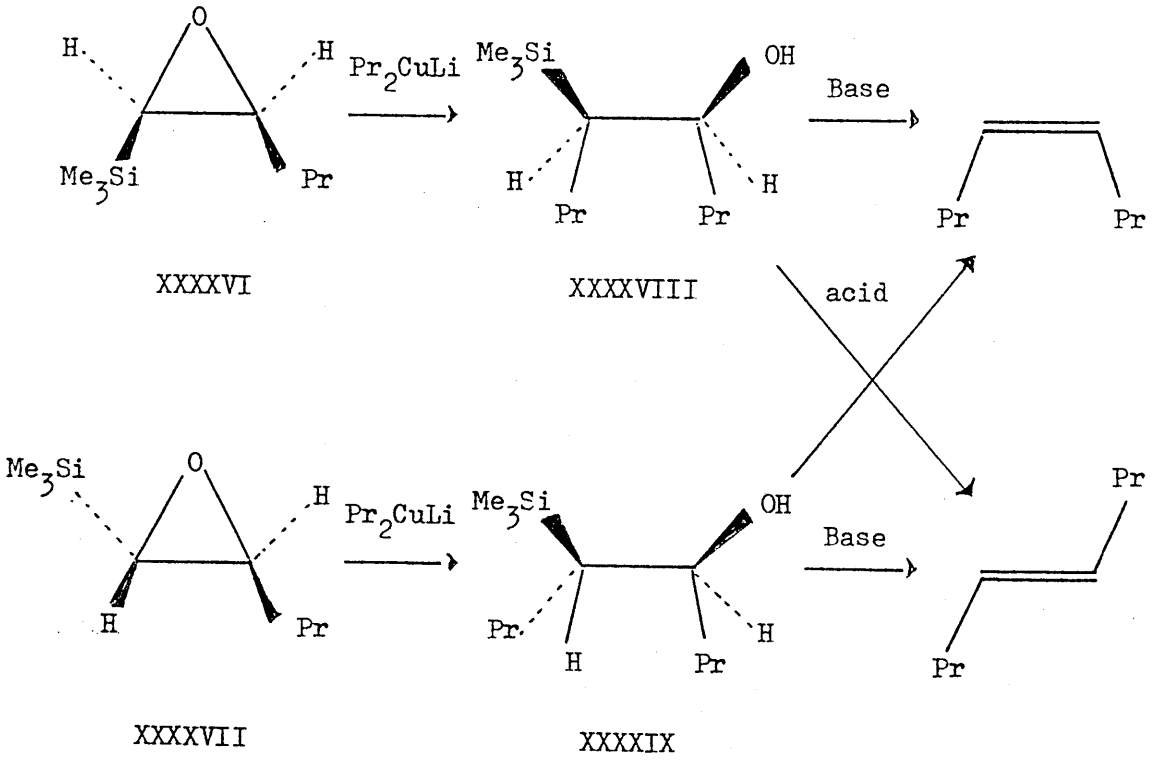
XXXXV



Support for this mechanism comes from the work of Peterson and Hudrlik.[92] They prepared diastereomerically pure samples of the β-hydroxysilanes XXXXVIII and XXXXIX by the addition of lithium

di-n-propylcuprate to the corresponding epoxysilanes XXXXVI and XXXXVII. It was found that treatment of the diastereomerically pure β-hydroxysilane with base or acid resulted in the stereospecific formation of either cis or trans 4-octene but never a mixture of olefins. This is illustrated in Scheme 19.

Scheme 19.

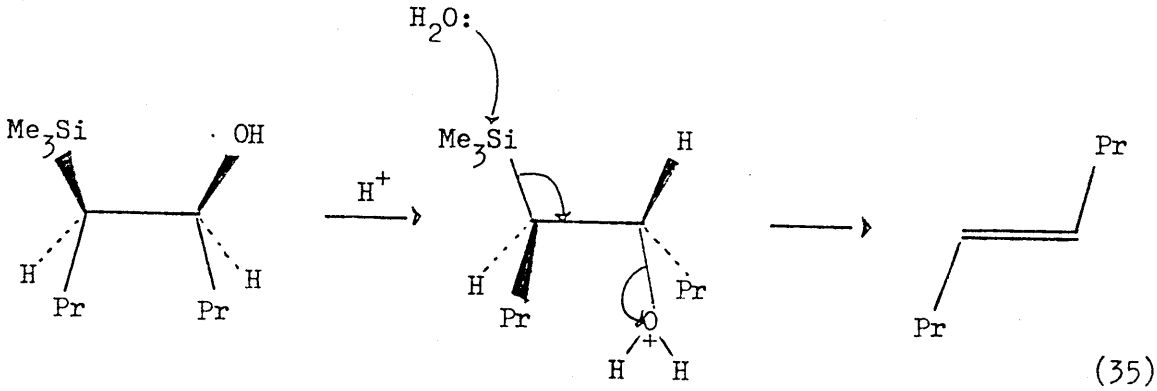


Treatment of XXXXVIII with base yields a β-silyl alkoxide which is the expected intermediate in the Peterson reaction. The formation of only the cis-octene from XXXXVIII is evidence that this intermediate undergoes syn elimination of silanolate and that the reaction is irreversible. If the reaction was reversible, treatment of XXXXVIII with base would result in the formation of some α-silyl carbanion and carbonyl compound. This would lead to detectable amounts of the trans olefin. However, only the cis olefin was obtained.

This contrasts with the experiments performed by Trippet[37] on the

β-hydroxyphosphonium iodide XII which gave a mixture of cis and trans olefin. These results indicate that the Wittig reaction is reversible whereas the Peterson reaction is not.

Treatment of XXXXVIII with acid yields only trans-4-octene as the result of anti elimination of silanol. The mechanism for this reaction is given in equation 35.



(35)

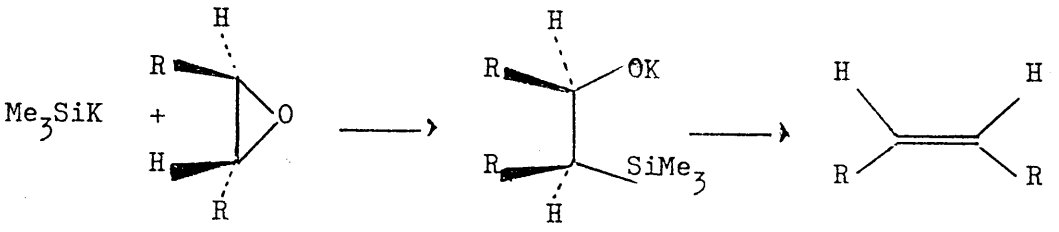
This is most probably a concerted elimination since treatment of XXXXIX with acid gave only cis olefin.

A similar result illustrating the irreversibility of the Peterson reaction was obtained when XXXXIX was treated with base. Similar evidence for the irreversible nature of the Peterson reaction was obtained by Dervan.[93] He reacted trimethylsilylpotassium with various epoxides and obtained the corresponding olefins. Typical results are given in Table 13.

Table 13. The Results of reactions between Trimethylsilylpotassium and various Epoxides.

Epoxide	% Yield of Olefin	% Product Geometry
trans-3-Hexene	99%	>99% cis
cis-3-Hexene	86%	>99% trans
trans-4-Octene	96%	>99% cis
cis-4-Octene	93%	>99% trans
2,5-Dimethyl-trans-3-Hexene	93%	>98% cis
2,5-Dimethyl-cis-3-Hexene	75%	>92% trans
trans-3-Methyl-2-Pentene	91%	>99% cis
cis-3-Methyl-2-Pentene	99%	>99% trans

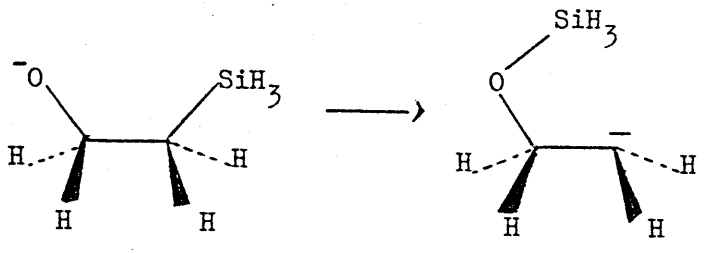
These results were explained by assuming backside attack of trimethylsilylpotassium on the cis (and trans) epoxides to generate threo-(and erythro) β-alkoxysilanes respectively. Syn elimination of the β-alkoxysilane proceeds to give only one olefin as the product. This is illustrated in equation 36. The isomeric purity of the product olefin is again indicative of the irreversibility of the Peterson reaction in this case.



(36)

The mechanism of the Peterson reaction has been examined, using CNDO calculations.[65] This investigation was carried out in the same manner as that of the Wittig reaction described earlier in section 1.3.

The results of these calculations suggested that the Peterson reaction does not proceed via a four centred dihydrooxasiletanide anion but via an intermediate alicyclic anion L. This decomposes to products with cleavage of the silicon carbon bond preceding that of the carbon oxygen bond, giving LI as a possible intermediate.



L LI

There is very little experimental evidence that reflects the advanced silicon carbon cleavage with respect to carbon oxygen cleavage. This is presumably because the carbon oxygen undergoes cleavage very rapidly after silicon carbon cleavage.

The stereochemistry of Peterson has been investigated by many research workers. When unsymmetrically substituted α-silyl carbanions react with aldehydes, cis or trans olefins can be produced. In many cases the cis:trans ratio of products is 1:1. However, some workers have carried out reactions in which the cis olefin has been favoured. Typical results obtained are given in Tables 14 and 15.

From these results there appear to be no obvious trends that reflect the factors which affect the cis:trans ratio of products. This is unlike the Wittig reaction where the pattern emerges that stabilized ylids give predominantly the trans olefins and non-stabilized ylids give the cis olefin in the absence of salts.

In recent years attempts have been made to improve the synthetic utility of the Peterson reaction with the aim of producing only one diastereoisomer of the olefin. One method of doing this is to trap the intermediate and thus isolate the β-hydroxysilane. If only one diastereoisomeric form of the β-hydroxysilane is isolated, treatment with base or acid should give the corresponding cis or trans olefin.

This approach has been used to generate diastereomerically pure forms of α,β-unsaturated esters.[100] When ethyl lithiotrimethylsilyl-acetate is reacted with carbonyl compounds at -78°C, the reaction proceeds directly to give the product olefin via an unstable β-silyl alkoxide. Under certain circumstances it is possible to stabilize the intermediate β-silyl alkoxide such that the corresponding

Table 14. The Results of Olefination of Carbonyl Compounds with α-Silyl Carbanions.

Carbanion	Carbonyl Compound	Olefin (cis:trans)		% Yield
$Ph_3Si\bar{C}H(CH_2)_4CH(CH_3)_2$	$CH_3(CH_2)_9CHO$	$(CH_3)_2CH(CH_2)_4CH{=}C_{10}H_{21}$	(1:1)	50%[88]
$Ph_3Si\bar{C}H(CH_2)_2CH_3$	PhCHO	$CH_3(CH_2)_2CH{=}CHPh$	(1:1)	50%[94]
$Ph_3Si\bar{C}HCH_2Ph$	PhCHO	$PhCH_2CH{=}CHPh$	(1:1)	40%[88]
$Me_3Si\bar{C}H\ Ph$	PhCHO	$PhCH{=}CHPh$	(1:1)	50%[75]
$Me_3Si\bar{C}HS(O)Ph$	$CH_2{=}CHCHO$	$CH_2{=}CHCH{=}CHS(O)Ph$	(1:1)	67%[95]
$Me_3Si\bar{C}HCN$	PhCHO	$PhCH{=}CHCN$	(1:1)	77%[78]
$Me_2PhSi\bar{C}(CH_3)CN$	$CH_3CH{=}CHCHO$	$CH_3CH{=}CHCH{=}C(CH_3)CN$	(1:1)	91%[96]
$Me_3Si\bar{C}HCO_2Et$	$CH_3(CH_2)_7CHO$	$CH_3(CH_2)_7CH{=}CHCO_2Et$	(1:1)	81%[77]
$Me_3Si\bar{C}HCO_2^-$	PhCHO	$PhCH{=}CHCO_2^-$	(1:1)	88%[97]

Table 15. The Results of Olefination of Carbonyl Compounds with α-Silyl Carbanions

Carbanion	Carbonyl Compound	Olefin (cis:trans)		% Yield
$Me_3Si\bar{C}HC{\equiv}CSiMe_3$	$CH_3(CH_2)_4CHO$	$CH_3(CH_2)_4C{=}CHC{\equiv}CSiMe$	(3:1)	77%[98]
$Me_3Si\bar{C}HP(O)(OEt)_2$	$(CH_3)_2CHCHO$	$(CH_3)_2CHCH{=}CHP(O)(OEt)_2$	(2:4:1)	92%[84]
t-$BuMe_2Si\bar{C}HCN$	$CH_3(CH_2)_4CHO$	$CH_3(CH_2)_4CH{=}CHCN$	(3:1)	62%[98]
$Me_3Si\bar{C}HCO_2^-$	$CH_3(CH_2)_4CHO$	$CH_3(CH_2)_4CH{=}CHCO_2^-$	(3:2)	90%[97]
$Me_3Si\bar{C}HCO_2Et$	PhCHO	$PhCH{=}CHCO_2Et$	(3:1)	84%[99]
$Me_3Si\bar{C}HCO_2Et$	CH_3COPh	$Ph(CH_3)C{=}CHCO_2Et$	(2:1)	63%[99]
$Me_3Si\bar{C}HS(O)Ph$	$(CH_3)_2CHCHO$	$(CH_3)_2CHCH{=}CHS(O)Ph$	(2:1)	30%[95]

hydroxy silyl ester can be obtained. This is achieved by generating the lithium silyl ester enolate using lithium diisopropylamine at -80°C followed by addition of 1 equivalent of magnesium bromide at -65°C. The reaction mixture is then cooled to -80°C prior to addition of the carbonyl compound. The change of counterion from lithium to magnesium stabilizes the intermediate β-silyl alkoxide, even at room temperature, and it can be easily hydrolysed to the corresponding β-hydroxysilane.

In each reaction only the intermediate LII was formed. The trans olefin was easily obtained by treatment of LIV with boron trifluoride. However, the formation of cis olefin was not achieved so readily. Treatment of LIV (R^1=Me,R^2=Ph) with sodium bis(trimethylsilyl)amide gave the cis and trans olefins in the ratio 10:90. The proportion of cis olefin was increased if hexamethylphosphoramide was added to the intermediate LII prior to hydrolysis, giving a cis:trans ratio of 80:20. Two explanations were put forward to account for the presence of the trans olefin. Firstly, the cis olefin could have been partially isomerized to the trans olefin. Secondly, the silicon could have been transferred from the carbon to the oxygen to give the β-substituted enolate LV, which would be followed by a β elimination to give a mixture of cis and trans olefin. The mechanism described and results obtained are given in Scheme 20 and Table 16.

Scheme 20.

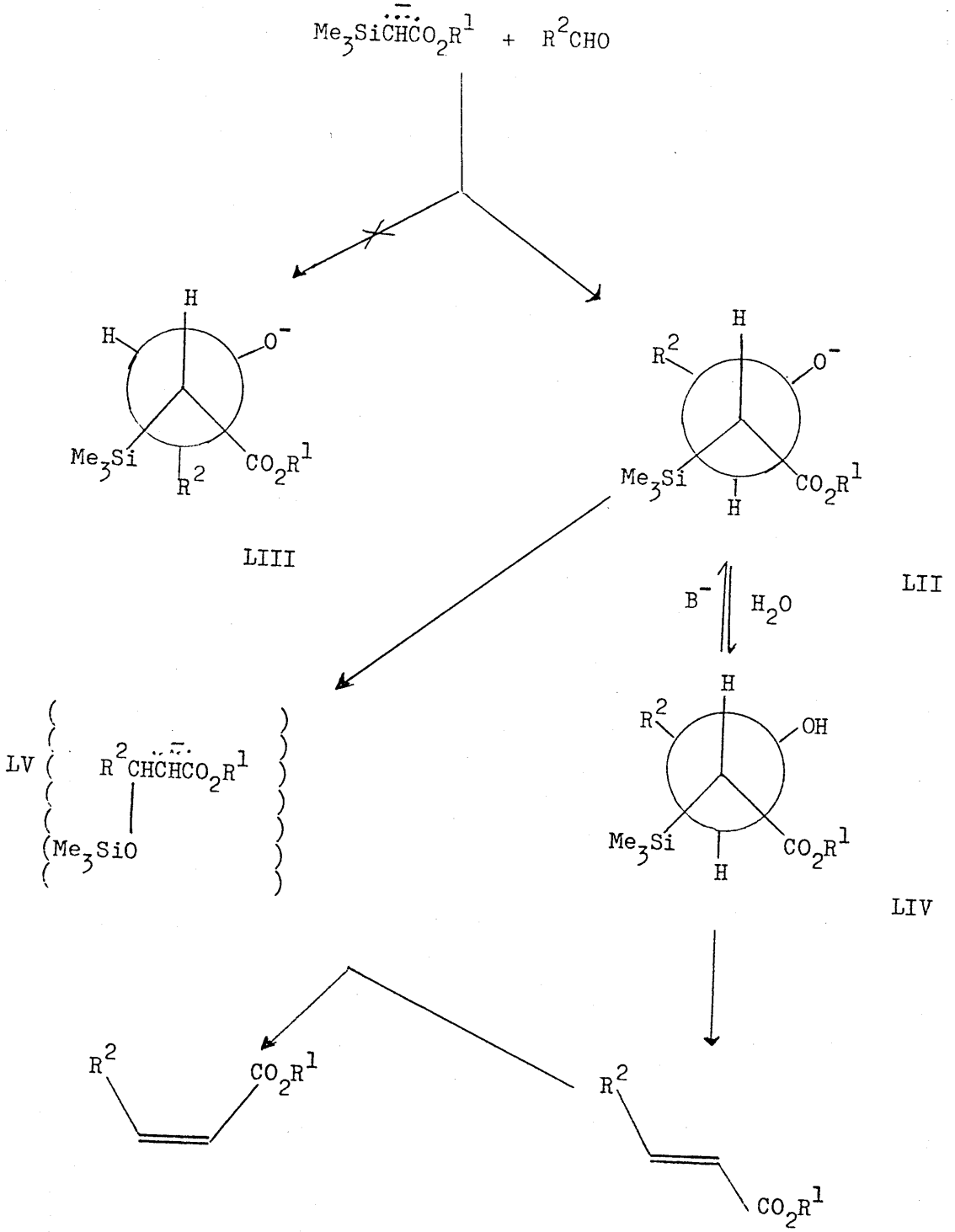

Me3SiCHCO2R1 + R2CHO
H
H
O-
Me3Si
R2
CO2R1
LIII
H
R2
O-
Me3Si
H
CO2R1
LII
B-
H2O
LV
R2CHCHCO2R1
Me3SiO
H
R2
OH
Me3Si
H
CO2R1
LIV
R2
CO2R1
R2
CO2R1

Table 16. The Synthesis of α,β-unsaturated esters.

Reaction Conditions [a]	R^1	R^2	% Yield of LII	% Yield of ester	cis:trans ratio
(A)	Me	Bu^n	76%	97%	2:98
(A)	Pr^i	PR^i	75%	100%	1:99
(A)	Me	Ph	78%	100%	1:99
(B)	Me	Bu^n		75%	85:15
(B)	Me	Ph		73%	80:20
(B)	Et	C_5H_{11}		65%	71:29

a (A): After hydrolysis. LIV was stirred for 1 hr with 1 equivalent of BF_3-OEt(in dichloromethane).

a (B): Before hydrolysis, hexamethylphosphoramide was added at 0°C and the mixture was stirred for 30 minutes.

The reaction of 1,3-bis(trimethylsilyl)propenyllithium LVI with carbonyl compounds is another example where the addition of magnesium bromide or trimethylborate to the reaction mixture has enhanced the production of one particular diastereomeric form of the olefin.

When 1,3-bis(trimethylsilyl)propenyllithium was reacted with carbonyl compounds in the absence of any additives, the reaction proceeded directly to give the corresponding diene.[101,102] The yield of the reaction was poor and a mixture of stereoisomers of 1-trimethylsilyl-buta-1,3-dienes was obtained. Typical results are given in Table 17.

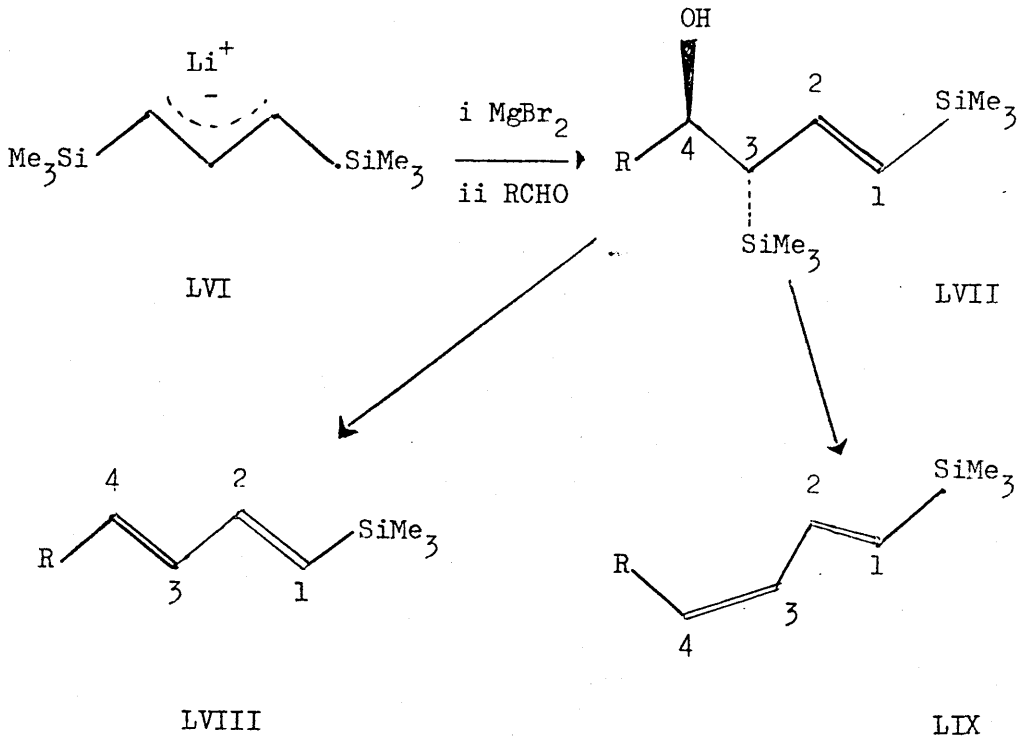
Table 17. The synthesis of 1-Trimethylsilylbuta-1,3-dienes from the Reaction of 1,3-bis(trimethylsilyl)propenyllithium[a] with aldehydes RCHO in the absence of additives.[102]

Aldehyde used	% Yield of diene	% Distribution of stereoisomers of butadiene			
		1 trans, 3 trans	1 trans, 3 cis	1 cis, 3 trans	1 cis, 3 cis
Pr^nCHO	34%	60%	40%	-	-
$n\text{-}C_8H_{17}CHO$	27%	73%	24%	3%	-
PhCHO	77%	77%	20%	3%	-

a = 1,3-bis(trimethylsilyl)propenyllithium was prepared using s-butyllithium in tetramethylethylenediamine/tetrahydrofuran solution at -76°C.

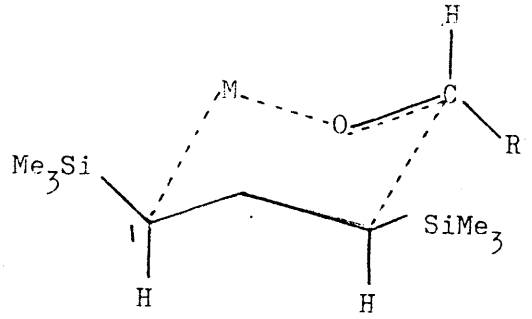
The β-hydroxy silane could be isolated if magnesium bromide was added to LVI prior to reaction with the carbonyl compound.[103] LVII was obtained in good yields and the reaction showed good stereoselectivity. In the case of benzaldehyde the major stereoisomer of LVII had the (3RS,4SR) stereochemistry and treatment with sulphuric acid or potassium hydride gave the dienes LVIII and LIX respectively as illustrated in Scheme 21.

Scheme 21.

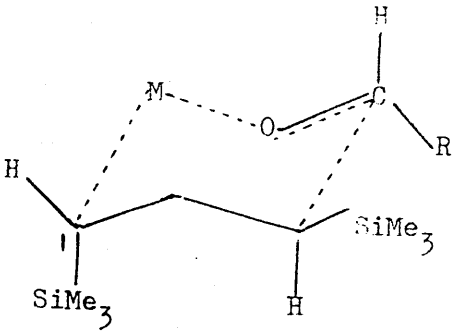


LVIII LIX

With aliphatic aldehydes, whilst the stereoselectivity for the formation of the C(3)-C(4) single bond in LVII remained high, the stereochemical integrity of the C(1)-C(2) double bond was diminished. This was discussed in terms of the formation of the cyclic transition states LX and LXI.



LX



LXI

M = MgBr

It was proposed that the stereochemistry at the C(1)—C(2) double bond of LVII would be governed by the relative proportions of LX and LXI. If the C(1)—C(2) double bond is to be cis, the trimethylsilyl group attached to C(1) would have to occupy an axial position LXI. Conversely, if the C(1)—C(2) double bond is to be trans, the trimethylsilyl group would have to occupy an equatorial position LX. From the results given in Table 18, it is apparent that when benzaldehyde is used the C(1)—C(2) double bond is nearly always trans. This indicates that transition state LX predominates. However, in the case of aliphatic aldehydes although LX is favoured, some LXI is formed, since about 25% of the diene contained a cis olefin at C(1).

When trimethyl borate was employed in place of magnesium bromide, the stereoselectivity of the reaction was further improved. In this case it was proposed that with a covalent carbon boron bond, the transition state LX, with the trimethylsilyl group occupying an equatorial position, becomes greatly preferred over LXI. These results are shown in Table 18.

Table 18. The Results of Synthesis of buta-1,3-dienes LVIX and LVIII from Reactions of LVI with aldehydes RCHO in the presence of magnesium bromide and trimethyl borate[103].

Additive	R	% Yield of LVII	Condition for LVII–LVIX or LVIII	% Yield of buta-1,3-dienes	% Distribution of stereoisomers of butadienes			
					1 trans,3 trans	1 trans,3 cis	1 cis,3 trans	1 cis,3 cis
$MgBr_2$	Pr^n	74%	H^+	94%	68%	3%	29%	-
			KH	94%	2%	68%	-	35%
	$n\text{-}C_8H_{17}$	80%	H^+	92%	72%	2%	26%	-
			KH	91%	1%	67%	-	32%
	Ph	80%	H^+	92%	90%	6%	4%	-
			KH	94%	9%	87%	-	4%
$B(OMe)_3$	Pr^n	52%	H^+	94%	92%	<1%	7%	-
			KH	94%	<1%	90%	-	9%
	$n\text{-}C_8H_{17}$	50%	H^+	95%	92%	<1%	7%	-
			KH	93%	<1%	90%	-	-
	Ph	50%	H^+	91%	84%	2%	15%	-
			KH	90%	6%	81%	-	13%

An alternative method of improving the stereochemical outcome of the Peterson reaction involves employing different trialkylsilyl groups together with the use of magnesium as the counterion. A combination of these factors was found to increase the proportion of the cis olefin in the product obtained from the reaction of metallated 1,3-bis(trimethylsilyl)propyne with carbonyl compounds.[98]

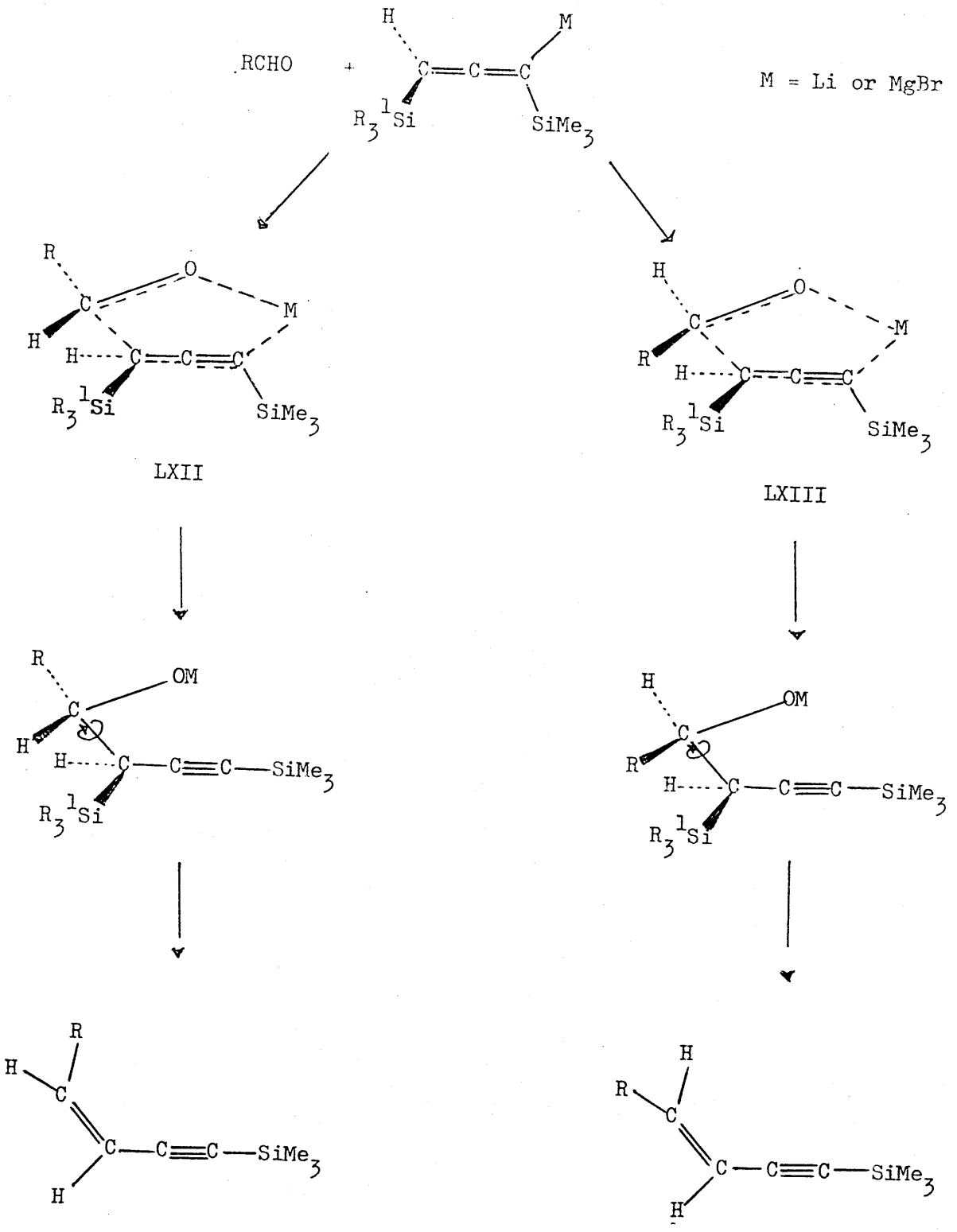
The metallation of the 1,3-bis(trimethylsilyl)propyne was performed at -78°C in dry tetrahydrofuran using t-butyllithium. To this magnesium bromide was added, if required, followed by the addition of the carbonyl compound. In this case the β-hydroxy silane was not isolated. The reaction mixture was stirred for 3 hrs at 50°C to ensure olefin formation was complete. When sterically large trialkylsilyl groups such as t-butyldimethylsilyl were employed the proportion of cis olefin increased as shown in Table 19. These results were explained by proposing the mechanism shown in Scheme 22.

The transition state LXII would be expected to be stabilized with respect to the transition state LXIII owing to the smaller steric interaction between trialkylsilyl group and the R group of the aldehyde. Thus increasing the steric bulk of the silyl group would favour LXII over LXIII and hence increase the proportion of cis olefin produced. It was also proposed that the use of magnesium as the counterion stabilized the formation of the cyclic transition state more than lithium.

Table 19. The Results of Enyne Synthesis from Disilylpropynes and Carbonyl Compounds

Carbonyl Compound	R_3Si	Counterion	% Yield of olefin	Olefin ratio cis:trans
$n\text{-}C_5H_{11}CHO$	Me_3Si	Li	77%	3:1
		MgBr	75%	7:1
	Et_3Si	Li	78%	6:1
		MgBr	89%	31:1
	$t\text{-}BuMe_2Si$	MgBr	65%	> 50:1
$C_6H_{11}CHO$	Me_3Si	Li	69%	8:1
		MgBr	84%	20:1
	Et_3Si	Li	88%	10:1
		MgBr	96%	23:1
	$t\text{-}BuMe_2Si$	Li	55%	12:1
		MgBr	75%	30:1
PhCHO	Me_3Si	Li	53%	1:1
		MgBr	76%	3:1
	Et_3Si	Li	63%	1:1
		MgBr	78%	2:1
	$t\text{-}BuMe_2Si$	MgBr	55%	1:1
PhCH=CHCHO	Me_3Si	MgBr	88%	2:1
	$t\text{-}BuMe_2Si$	MgBr	90%	7:1

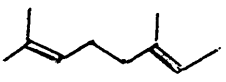
Scheme 22.



To test the generality of the mechanism shown in Scheme 22, the synthesis of α,β-unsaturated nitriles was also investigated.[98] This particular system was chosen because it was believed that the carbanion derived from α-silylated acetonitrile would react in a similar manner to metallated 1,3-bis(trimethylsilyl)propyne.

The α-silyl carbanion was generated using lithium diisopropylamide at -78°C. To this was added magnesium iodide followed by the addition of the carbonyl compound. The intermediate β-hydroxy silane was not isolated. The reaction mixture was stirred at 50°C for 1 hr to ensure complete olefin formation. The results obtained are given in Table 20.

Table 20. The Results of Synthesis of α,β-unsaturated Nitriles.

Carbonyl Compound	Reagent used	% Yield of olefin	Olefin Ratio cis:trans
$C_6H_{11}CHO$	t-$BuMe_2SiCH_2CN$	76%	6:1
	Ph_3SiCH_2CN	80%	9:1
$C_5H_{11}CHO$	t-$BuMe_2SiCH_2CN$	62%	3:1
	Ph_3SiCH_2CN	63%	5:1
	t-$BuMe_2SiCH_2CN$	79%	2:1
	Ph_3SiCH_2CN	85%	2:1

These results again indicate that the presence of sterically bulky groups on silicon, in conjunction with a magnesium counterion, increase the proportion of cis olefin that is formed.

1.8 Comparison of the Wittig and Peterson Reactions

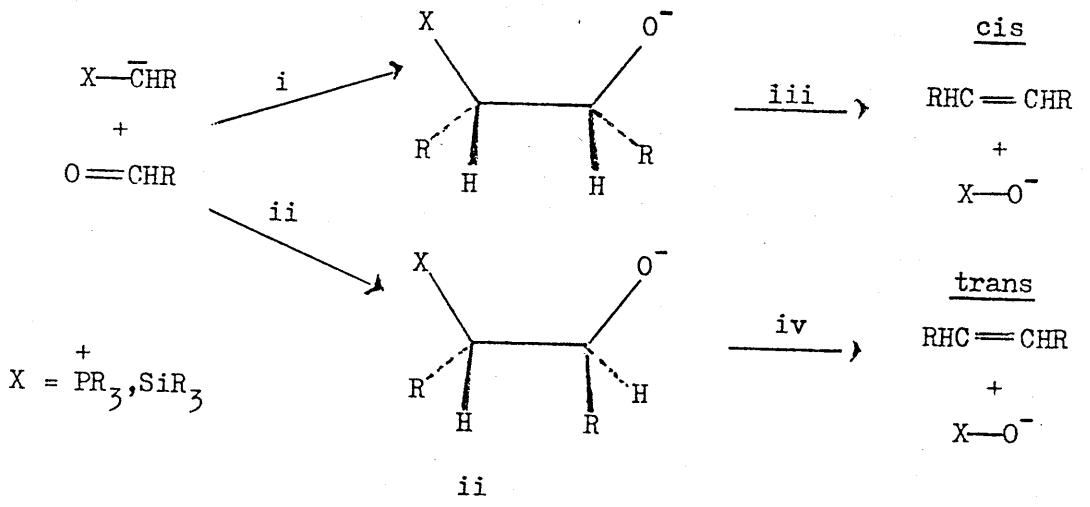
The Wittig and Peterson reactions are both methods of carbonyl olefination and therefore one could expect certain similarities in the possible mechanisms of these reactions. Both mechanisms can be represented by Scheme 23 in which the reactants combine to give two diastereomeric intermediates that decompose to give either cis or trans olefins. The similarities and differences of these reactions will be discussed under three headings;

i The combination of reactants.

ii The nature of the intermediate.

iii The decomposition of the intermediate to products.

Scheme 23.



ii

i The Combination of Reactants

The mechanism proposed by Speziale and Bissing[36] involved the slow reversible combination of the reactants to give a betaine. The degree of reversibility of this reaction was believed to be dependent on the nature of the ylid used. If the ylid was stabilized the reaction was thought to be more reversible than if the ylid was unstabilized. It

was believed that the greater the reversibility, the more the trans olefin would be favoured.[35] The preparation of cis olefins from non-stabilized ylids has been explained by proposing that the reaction is much less reversible and proceeds via an early transition state.[47-49]

Other proposals have been suggested that involve a cycloaddition mechanism. In the case of non-stabilized ylids this was believed to be a $\pi^2_a + \pi^2_s$[51] cycloaddition giving a predominance of the cis oxaphosphetane. In contrast, a stabilized ylid was believed to undergo a $\pi^2_s + \pi^2_s$[55] cycloaddition giving a predominance of trans oxaphosphetane.

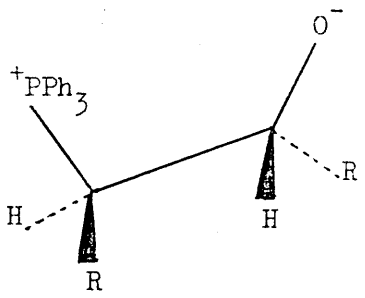
A variation of the cycloaddition mechanism has been proposed by Bestmann.[60] He believed that the ylid and carbonyl compound reacted via a betaine-like transition state to give only the cis oxaphosphetane. The first step of this mechanism was believed to be independent of nature of the ylid and that a cis oxaphosphetane was produced when either a stabilized or a non-stabilized ylid was employed.

In contrast to the Wittig reaction, the combination of reactants for the Peterson reaction appears to be a straightforward nucleophilic attack of an α-silyl carbanion on a carbonyl compound which has been shown to be irreversible.[92] The possibility of a cycloaddition mechanism for the Peterson reaction would be very unlikely since there is no formal silicon carbon double bond.

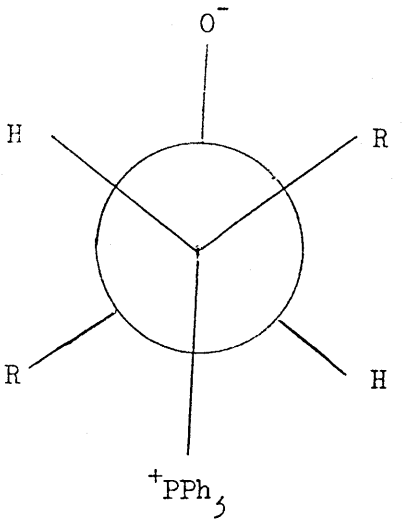
ii The Nature of the Intermediate

It has been proposed that the intermediate in the Wittig reaction may be a betaine or an oxaphosphetane. In the case of the betaine it is believed to be formed in the synclinal conformation LXIV when a stabilized ylid reacts with a carbonyl compound.[36] In contrast to this,

the anti-periplanar conformation LXV is believed to be formed initially when a non-stabilized ylid reacts with a carbonyl compound.[47]



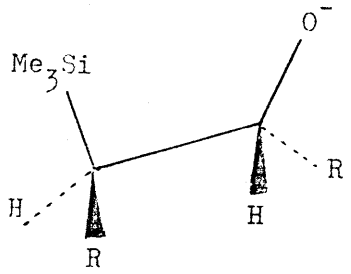
LXIV



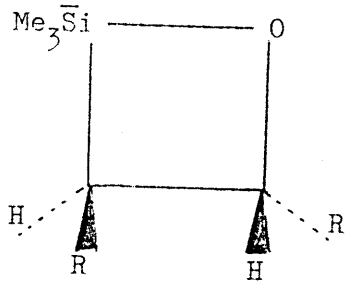
LXV

Depending on the mechanism proposed, it is believed that cis or trans oxaphosphetanes can be produced. Oxaphosphetanes have been observed using low temperature n.m.r. Attempts to determine whether betaines and oxaphosphetanes are in equilibrium with one another have given inconclusive results. The work of Schlosser[57] indicates that such an equilibrium exists but the work of Corey[59] suggests that it does not. The systems studied are given in Schemes 12 and 13.

Less is known about the nature of the intermediate in the Peterson reaction, though it is generally believed to be an acylic anion LXVI rather than the cyclic four centred oxasiletanide anion LXVII. No proposals have been put forward as to whether LXVI is formed in an anti-periplanar or syn-periplanar conformation. This presumably would be dependent on the nature of the R groups and the strength of silicon oxygen interaction in the transition state.



LXVI



LXVII

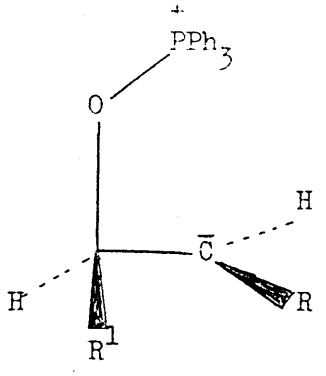
Unlike the Wittig reaction, the intermediate of the Peterson can be trapped as a β-hydroxysilane.[75] Subsequent treatment of the β-hydroxysilane with base yields the product olefin. The preparation of diastereomerically pure β-hydroxysilanes has enabled further insight into the nature of elimination of silanolate and the formation of the olefin product.

iii The Decomposition of the Intermediate to Products.

Most mechanisms proposed to explain the Wittig reaction, assume that triphenylphosphine oxide is the result of a syn elimination which occurs in a synchronous manner.[35] The proportion of cis or trans olefins being produced being dependent on other factors.

However, Bestmann[60] proposed a mechanism in which the intermediate produced was always the cis oxaphosphetane. He also proposed that the elimination of triphenylphosphine was not a synchronous event but that the phosphorus carbon bond undergoes cleavage before the carbon oxygen bond giving LXVIII as an intermediate. In this case the product controlling factor is the rate of rotation versus the rate of elimination. If R is an electron donor, such as alkyl, a very rapid elimination of triphenylphosphine oxide occurs to give cis olefin. If R is an electron acceptor such as an ester group, the lifetime of LXVIII is increased allowing rotation about the carbon-

carbon bond enabling trans olefin to be formed.



LXVIII

In the case of the Peterson reaction the treatment of diastereomerically pure β-hydroxysilane with base has shown that the elimination of silanolate takes place in a syn fashion and is a synchronous event. Although the CNDO calculations of Carey's do indicate that silicon carbon bond cleavage is advanced with respect to carbon oxygen cleavage, there is very little experimental evidence to support this. There is also no observable trend in the cis:trans ratios of the product olefins on varying the nature of the starting α-silyl carbanion from stabilized to non-stabilized.

From this survey of the literature it would appear that the stereochemical outcome of the Wittig reaction is controlled by many factors. In contrast, it would appear that the stereochemistry of the olefins produced as the result of a Peterson reaction is mainly determined by the initial approach of an α-silyl carbanion to a carbonyl compound.

Chapter 2 EXPERIMENTAL

2.1 Materials used

Spectroscopic data were obtained using the following spectrometers: i.r., Pye Unicam SP 1050; n.m.r., Jeol FX90Q. All n.m.r. spectra were referenced to TMS=0. Mass spectra were obtained courtesy of Hoechst Pharmaceuticals Ltd. using a Cresta M.S.30. Elemental analyses were obtained courtesy of Butterworth Ltd. G.l.c. were performed using a Pye Unicam series 204 chromatograph with a flame ionisation detector coupled to a Cambridge 308 integrator. Melting points were measured using a Buchi 510. Column chromatography was carried out using silica gel 60, t.l.c. grade, supplied by Merck. The eluting solvent was glass distilled hexane obtained from Rathburn Chemicals Ltd. The Peterson reactions studied were performed in a Faircrest nitrogen dry box.

Hexamethylphosphoramide.- A commercial sample (Aldrich Chemical Co., Ltd.) was distilled under reduced pressure from phosphorus pentoxide, boiling at 75°C-77°C at 1mm of mercury prior to use.

Benzaldehyde.- A commercial sample (Aldrich Chemical Co.,Ltd.) was distilled under reduced pressure, boiling at 50-53°C at 8mm of mercury and stored under nitrogen prior to use.

Dimethylformamide.- A gold label grade sample (Aldrich Chemical Co., Ltd.) was used without further purification.

Dimethylsulphoxide.- A gold label grade sample (Aldrich Chemical Co., Ltd.) was used without further purification.

Sodium tetraphenylboron.- A commercial sample (Aldrich Chemical Co., Ltd.) was used without further purification.

Lithium iodide.- A commercial sample (Alfa chemicals Ltd.) was used without further purification.

Lithium perchlorate.- A commercial sample (B.D.H. Chemicals Ltd.) was used without further purification.

Tetrahydrofuran.- A commercial sample (B.D.H. Chemicals Ltd.) was dried by distillation from calcium hydride at 760mm of mercury prior to use.

Diethyl Ether.- A commercial sample (B.D.H. Chemicals Ltd.) was dried by distillation from calcium hydride at 760mm of mercury prior to use.

2.2 Preparation of Compounds

Preparation of Tri(p-methylphenyl)silane.- This was prepared by the method of Benkeser[104] to give a product m.p. 83-84°C (lit.[104], m.p. 82.5-83.5°C).

Preparation of Tri(p-methoxyphenyl)silane.- This was prepared by the method of Benkeser[104] to give a product m.p. 72-74°C (lit.[104], m.p. 74°C).

Preparation of Tri(m-fluorophenyl)silane.- This was prepared by the method of Eaborn[105] to give a product with b.p. 148-150°C at 0.7mm of mercury, (lit.[105], 148-151/0.8mm Hg.)

Preparation of Benzyltri(p-trifluoromethylphenyl)silane.- This was prepared by the method of Brook[106] to give a product m.p. 138°C (lit.[106], m.p.138-40°C).

Preparation of Dicyclohexylmethylsilane.- This was prepared by the method of Sultanov[107] et al to give a product with a b.p. 94-96°C at 0.4mm of mercury (lit.[107], b.p. 102-104/0.5mm Hg).

Preparation of Diisobutylmethylsilane.- This was prepared by the method of Ergorochkin[108] to give a product with b.p. 158-161°C at 760mm of mercury (lit.[108], b.p. 159.8°C/760mm mercury).

Preparation of Benzyltrimethylsilane.- This was prepared by the method of Hauser[109] to give a product with b.p. 38-39°C at 1.5mm of mercury (lit.[109], 95°C/35mm mercury).

Preparation of Bis(trimethylsilyl)phenylmethane.- This was prepared by the method of Dunogues[110] et al to give a product with b.p. 76-80°C at 1mm of mercury (lit.[111], 103-104°C/6.5mm mercury).

Preparation of Phenyl(triethylsilyl)(trimethylsilyl)methane.- A 1.55M solution of butyllithium in hexane ($60cm^3$, 95mmol) was added to benzyltrimethylsilane (15g, 90mmol) in tetramethylethylenediamine ($12cm^3$) and diethyl ether ($20cm^3$) under nitrogen. To this was added chlorotriethylsilane (13.5g, 90mmol) and the reaction mixture refluxed for 10 minutes. This was quenched with 2M hydrochloric acid ($5cm^3$) followed by washing with 2M hydrochloric acid ($2x10cm^3$) and then with saturated sodium hydrogen carbonate solution ($2x10cm^3$). The aqueous extracts were washed with diethyl ether ($20cm^3$) and the ethereal extract combined with that of the reaction mixture. The ethereal solution was dried over sodium sulphate and the solvent removed on a rotary evaporator. The residue was distilled at reduced pressure to give the product phenyl(triethylsilyl)(trimethylsilyl)methane (10.7g, 43%) b.p. 81-85°C(0.4-0.5mm Hg): Anal. Calcd. for $Si_2C_{16}H_{30}$:C,68.96; H,10.86; Si,20.18. Found C,69.13; H,10.89; Si N/D. I.R. (liquid film) ν_{max} 2960, 2890, 1590, 1490, 1245, 1195, 1030, 1010, 900cm^{-1}, ^1H n.m.r., $CDCl_3$, δ 0.07(s,9H), 1.1-0.52(m,15H), 1.7(s,1H), 7.7.2(m,5H), ^{13}C n.m.r., $CDCl_3$, 0.66, 5.33, 8.24, 26.63, 125.3, 130.1, 131.2, 145.17p.p.m., ^{29}Si n.m.r. $CDCl_3$, 1.5, 6.69.p.p.m. Mass spectrum M^+ 278.19, M^+-15 263.16, M^+-163 135.07

Preparation of Phenyl(dicyclohexylmethylsilyl)(trimethylsilyl)-methane.- Dicyclohexylmethylsilane (15g,71mmol) was added to ice cold carbon tetrachloride ($200cm^3$) and chlorine bubbled through the solution until the Si-H ^{1}Hn.m.r. signal disappeared. The solvent was removed on a rotary evaporator to give chlorodicyclohexylmethylsilane (15.5g) which was used immediately at the next stage. A 1.55M solution of n-butyllithium in hexane ($45cm^3$,70mmol) was added to benzyltrimethylsilane (11g,67mmol) in tetramethylethylenediamine ($10cm^3$) and diethyl ether ($20cm^3$) under nitrogen. To this chlorodicyclohexylmethylsilane (15.5g,70mmol) was added and the reaction mixture refluxed for 30 minutes. This was quenched with 2M hydrochloric acid ($5cm^3$) followed by washing with 2M hydrochloric acid ($2x10cm^3$) and then with saturated sodium hydrogen carbonate solution ($2x10cm^3$). The aqueous extracts were washed with diethyl ether ($20cm^3$) and the ethereal extract combined with that of the reaction mixture. The ethereal solution was dried over sodium sulphate and the solvent removed on a rotary evaporator. The residue was distilled twice to give the product phenyl(dicyclohexylmethylsilyl)(trimethylsilyl)methane (3.1g,19%)b.p.165°C.(0.5mmHg): Anal Calcd for $Si_2C_{23}H_{40}$: C,74.11; H,10.8; Si,15.09. Found C,74.38; H,10.78; Si,N/D. I.R. (liquid film) ν_{max}2930, 2850, 1600, 1495, 1450, 1250, 1195, 1035, 850cm^{-1}. ^{1}H n.m.r., $CDCl_3$, δ 0.05 (s,12H), 1.2-1.8 (m,23H), 6.9-7.2(m,5H), ^{13}C n.m.r., $CDCl_3$,-5.04,0.92, 24.7, 25.9, 26.9, 27.5, 28.9, 123.7, 128.3, 129.8, 143.5p.p.m. ^{29}Si n.m.r., $CDCl_3$, 1.73p.p.m. Mass spectrum M^+ 372.27, M^+-15 357.25, M^+-83 289.18, M^+-163 210.18.

Preparation of Phenyl(diisobutylmethylsilyl)(trimethylsilyl)methane.- Diisobutylmethylsilane (15g,94mmol) was added to ice cold carbon tetrachloride ($200cm^3$) and chlorine bubbled through the solution until the Si-H ^{1}Hn.m.r. signal disappeared. The solvent was removed on a rotary evaporator to give diisobutylchloromethylsilane (18g) which was used immediately at the next stage. A 1.55M solution of n-butyllithium in hexane ($60cm^3$,90mmol) was added to benzyltrimethylsilane (15g,90mmol) in tetramethylethylenediamine ($12cm^3$) and diethyl ether ($20cm^3$) under nitrogen. To this was added diisobutylchloromethylsilane (18g,90mmol) and refluxed for 30 minutes. This was quenched with 2M hydrochloric acid ($5cm^3$) followed by washing with 2M hydrochloric acid ($2x10cm^3$) and then with saturated sodium hydrogen carbonate solution ($2x10cm^3$). The aqueous extracts were washed with diethyl ether ($20cm^3$) and the ethereal extract combined with that of the reaction mixture. The ethereal solution was dried over sodium sulphate and the solvent removed on a rotary evaporator. The residue was distilled twice to give the product phenyl(diisobutylmethylsilyl)-(trimethylsilyl)methane (6.4g,22%) b.p.110-115°C(0.3-0.5mm Hg): Anal Calcd for $Si_2C_{19}H_{36}$: C,71.15; H,11.32; Si 17.53. Found C,71.16; H,11.3; Si N/D. I.R. (liquid film) ν_{max} 2980, 2870, 1600, 1495, 1250, 1195, 1010, 850cm^{-1}.^{1}H n.m.r., $CDCl_3$, δ 0.02-0.13(m,12H), 0.72-1.78 (m,19H), 7-7.2 (m,5H),^{13}C n.m.r., $CDCl_3$,-4.65, 0.49, 13.76, 20.53, 21.6, 25.14, 123.3, 127.9, 129.4, 142.9p.p.m. ^{29}Si n.m.r., $CDCl_3$,1.73, 5.87p.p.m. Mass spectrum M^+ 320.24, M^+-15 305.21, M^+-57 263.16, M-163, 157.14.

Preparation of Phenyl(t-butyldiphenylsilyl)(trimethylsilyl)methane.- A 1.55M solution of butyllithium in hexane ($40cm^3$,62mmol) was added to benzyltrimethylsilane (10g,60mmol) in tetramethylethylenediamine ($9cm^3$) and diethyl ether ($20cm^3$) under nitrogen. To this was added t-butylchlorodiphenylsilane (14.3g,60mmol) and the reaction mixture refluxed for 30 minutes. This was quenched with 2M hydrochloric acid ($5cm^3$) followed by washing with 2M hydrochloric acid ($2x10cm^3$) and then with saturated sodium hydrogen carbonate solution ($2x10cm^3$). The aqueous extracts were washed with diethyl ether ($20cm^3$) and the ethereal extract combined with that of the reaction mixture. The ethereal solution was dried over sodium sulphate and the solvent removed on a rotary evaporator. The residual oil was recrystallized from 40°C-60°C petroleum ether to give the product phenyl(t-butyl-diphenylsilyl)(trimethylsilyl)methane (6.7g,27%) prisms m.p. 102-104°C Anal. Calcd for $Si_2C_{26}H_{34}$: C,77.57; H,8.52; Si,13.96. Found C,77.56; H,8.59; Si,13.96. I.R.(nujol mull) ν_{max} 1600, 1500, 1260, 1205, 910cm^{-1}, ^1H n.m.r., $CDCl_3$, δ-0.36 (s,9H), 0.68 (s,9H), 2.38 (s,1H), 7.2-7.7 (m,15H), ^{13}C n.m.r., $CDCl_3$, 0.43, 20.48, 25, 28.5, 124.22, 127.31, 127.85, 128.34, 129.26, 129.59, 137.06, 137.6, 141.94 p.p.m. ^{29}Si n.m.r., $CDCl_3$,-7.16, 2.02 p.p.m. Mass spectrum M^+ 402.22, M^+-15 387.2, M^+-57 345.15.

Preparation of Phenyl(diphenylmethylsilyl)(trimethylsilyl)methane.- A 1.55M solution of butyllithium in hexane ($40cm^3$,62mmol) was added to benzyltrimethylsilane (10g,60mmol) in tetramethylethylenediamine ($9cm^3$) and diethyl ether ($20cm^3$) under nitrogen. To this was added chlorodiphenylmethylsilane and the reaction mixture refluxed for 30 minutes. This was quenched with 2M hydrochloric acid ($5cm^3$) followed by washing with 2M hydrochloric acid ($2x10cm^3$) and then with saturated sodium hydrogen carbonate solution ($2x10cm^3$). The aqueous extracts were washed with diethyl ether ($20cm^3$) and the ethereal extract combined with that of the reaction mixture. The ethereal solution was dried over sodium sulphate and the solvent removed on a rotary evaporator. The residue was recrystallized using hexane to give the product phenyl(diphenylmethylsilyl)(trimethylsilyl)methane (4.6g,22%) prisms m.p. 45-47°C: Anal. Calcd for $Si_2C_{23}H_{28}$: C,76.66; H,7.84; Si,15.81. Found C,76.6; H,7.89; Si N/D. I.R. (nujol mull) ν_{max} 1590, 1480, 1425, 1250, 1200, 1105, 1030, 910, 840cm^{-1}, ^1H n.m.r., $CDCl_3$, δ 0.02(s,9H), 0.03(s,3H), 2.35(s,1H), 7.1-75(m,15H), ^{13}C n.m.r., $CDCl_3$, -2.36, 0.11, 27.29, 123.63, 127.42, 127.76, 128.1, 128.8, 129.25, 129.43, 138.82, 135.06, 137.41, 141.84 p.p.m. ^{29}Si n.m.r., $CDCl_3$, -9.49, 2.58 p.p.m. Mass spectrum M^+360.19, M^+-15 345.16, M^+-163 197.95.

Preparation of Bis(dimethylphenylsilyl)phenylmethane.- A 1.55M solution of butyllithium in hexane ($30cm^3$,45mmol) was added to benzyldimethylphenylsilane (10g,45mmol) in tetramethylethylenediamine ($10cm^3$) and diethyl ether ($20cm^3$) under nitrogen. To this was added chlorodimethylphenylsilane (7.6g,45mmol) and the reaction mixture refluxed for 20 minutes. This was quenched with 2M hydrochloric acid ($5cm^3$) followed by washing with 2M hydrochloric acid ($2x10cm^3$) and then with saturated sodium hydrogen carbonate solution ($2x10cm^3$). The aqueous extracts were washed with diethyl ether ($20cm^3$) and the ethereal extract combined with that of the reaction mixture. The ethereal solution was dried over sodium sulphate and the solvent removed on a rotary evaporator. The residual oil was distilled twice at reduced pressure to give the product bis(dimethylphenylsilyl)phenylmethane (7.9g,47%) b.p.165-169°C (0.03-0.05mmHg): Anal.Calcd for $Si_2C_{23}H_{28}$: C,76.66; H,7.84; Si,15.6. Found C,76.63; H,7.96; Si,N/D. I.R. (liquid film) ν_{max} 2950, 1590, 1490, 1425, 1245, 1195, 1110, 905cm^{-1}, ^1H n.m.r., $CDCl_3$, δ 0.18(s,6H), 0.29(s,6H), 2.05(s,1H), 7-7.45(m,15H), ^{13}C n.m.r., $CDCl_3$, -6.78, -6.2, 25.79, 126.27, 130.4, 130.92, 131.78, 131.78, 132.24, 137.24, 142.75, 145.57 p.p.m. ^{29}Si n.m.r., $CDCl_3$, -3.54 p.p.m. Mass spectrum M^+ 360.19.

Preparation of Phenyl(dimethylphenylsilyl)(trimethylsilyl)methane.- A 1.55M solution of butyllithium in hexane ($35cm^3$,55mmol) was added to benzyltrimethylsilane (8g,50mmol) in tetramethylethylenediamine ($9cm^3$) and diethyl ether ($20cm^3$) under nitrogen. To this was added chlorodimethylphenylsilane (8.5g,50mmol) and the reaction mixture refluxed for 10 minutes. This was quenched with 2M hydrochloric acid ($5cm^3$) followed by washing with 2M hydrochloric acid ($2x10cm^3$) and then with saturated sodium hydrogen carbonate solution ($2x10cm^3$). The aqueous extracts were washed with diethyl ether ($20cm^3$) and the ethereal extract combined with that of the reaction mixture. The ethereal solution was dried over sodium sulphate and the solvent removed on a rotary evaporator. The residue was distilled at reduced pressure to give the product phenyl(dimethylphenylsilyl)-(trimethylsilyl)methane (8.1g,57%) b.p.132-136°C (0.05mmHg): Anal. Calcd for $Si_2C_{18}H_{26}$: C,72.39; H,8.79; Si,18.83. Found C,72.3; H,8.63; Si N/D. I.R. (liquid film) ν_{max} 2950, 2895, 1600, 1490, 1425, 1250, 1200, 1110, 905, 690cm^{-1}. ^1H n.m.r., $CDCl_3$,δ-0.08(s,9H), 0.32(s,3H), 0.5(s,3H), 1.83(s,1H), 6.9-7.6 (m,10H), ^{13}C n.m.r., $CDCl_3$, -1.25, -0.81, 0.595, 29.74, 124, 128.1, 128.6, 129.4, 129.5, 134.5, 140, 143 p.p.m. ^{29}Si n.m.r., $CDCl_3$, -3.812, 2.057 p.p.m. Mass spectrum M^+ 298.16, M^+-15 283.14, M^+-163 135.07.

Preparation of Benzyldimethylphenylsilane.- Benzyl chloride (12g, 95mmol) was added to magnesium turnings (2.4g,100mmol) in tetrahydrofuran ($150cm^3$). After the Grignard reagent had been formed chlorodimethylphenylsilane (16g,95mmol) was added and the reaction mixture refluxed for 1 hour. The reaction mixture was quenched by addition of saturated ammonium chloride ($5cm^3$) and the magnesium salts were filtered off. The solvent was dried over sodium sulphate and removed on a rotary evaporator. The residue was distilled at reduced pressure to give the product benzyldimethylphenylsilane (11.2g, 52%) b.p.112-115°C (0.1mmHg): Anal. Calcd for Si $C_{15}H_{18}$: C,79.55; H,8.02; Si,12.42. Found C,79.55; H,7.95; Si, N/D. I.R. (liquid film) ν_{max} 3020, 2950, 1600, 1495, 1435, 1250, 1205, 1155, 1115, 1055, 830, 690cm^{-1}. ^1H n.m.r.,δ $CDCl_3$, 0.44(s,6H), 2.48(s,2H), 7.1-7.7(m,10H), ^{13}C n.m.r., $CDCl_3$, -3.41, 26.2, 124.1, 127.74, 128.1, 128.33, 128.72, 129.04, 133.78 p.p.m., ^{29}Si n.m.r., $CDCl_3$, -3.56 p.p.m. Mass spectrum M^+ 226.23, M^+-135 91.1.

Preparation of Phenyl(tris(p-trifluoromethylphenyl)silyl)(trimethylsilyl)methane.- A 1.55M solution of butyllithium in hexane ($10cm^3$, 16mmol) was added to benzyltri(p-trifluoromethylphenyl)silane (6.5g, 12mmol) in hexamethylphosphoramide ($25cm^3$) and tetrahydrofuran ($25cm^3$) under nitrogen. To this was added chlorotrimethylsilane (2g,20mmol) and the reaction mixture warmed for 5 minutes. The reaction was quenched with 2M hydrochloric acid ($5cm^3$) followed by addition of diethyl ether ($50cm^3$). The reaction mixture was washed with iced concentrated hydrochloric acid ($3x25cm^3$) and then with saturated sodium hydrogen carbonate solution ($3x25cm^3$). The organic layer was dried over sodium sulphate and the solvent removed on a rotary evaporator. Purification of the residual oil was by column chromatography (hexane, t.l.c. grade silica) to give the product phenyl-(tris(p-trifluoromethylphenyl)silyl)(trimethylsilyl)methane (2.3g, 27%) m.p. 116-117°C, prisms: Anal. Calcd for $Si_2C_{31}H_{27}F_9$: C,59.39; H,4.34; F,27.3; Si,8.97. Found C,59.47; H,4.49; F,25; Si,N/D. I.R. (nujol mull) ν_{max} 1600, 1390, 1250, 1195, 1165, 1120, 1060, 1015, 840, 820 cm^{-1}. ^1H n.m.r., $CDCl_3$,δ0(s,9H), 2.61(s,1H), 6.8-7.5(m,18H). ^{13}C n.m.r., $CDCl_3$, 0.11, 26.11, 118.0, 124.3, 124.6, 128.7, 130.1, 131.2, 136.4, 139.34, 139.5 p.p.m. ^{29}Si n.m.r., $CDCl_3$, 2.68, -12.86 p.p.m. Mass spectrum M^+-73 553.13, M^+-163 463.07.

Preparation of Benzyltri(m-fluorophenyl)silane.- Tri(m-fluorophenyl)silane (30g,95mmol) was dissolved in ice cold carbon tetrachloride ($200cm^3$) and chlorine bubbled through the solution until the Si-H, ^1H n.m.r. signal disappeared. The solvent was removed on a rotary evaporator to give chlorotri(m-fluorophenyl)-silane (31g) which was used immediately at the next stage. Benzyl chloride (12g,95mmol) was added to magnesium turnings (2.4g,100mmol) in tetrahydrofuran ($100cm^3$). After the Grignard reagent had been formed chlorotri(m-fluorophenyl)silane (30g,90mmol) was added and the reaction mixture refluxed for 1 hour. The reaction mixture was quenched by addition of saturated ammonium chloride ($5cm^3$) and the magnesium salts were filtered off. The solvent was dried over sodium sulphate and removed on a rotary evaporator. Purification of the residual oil was achieved by column chromatography (hexane, t.l.c. grade silica) to give the product benzyltri(m-fluorophenyl)-silane (8.7g,24%) m.p. 67-69°C prisms: Anal. Calcd for Si $C_{25}H_{19}F_3$: C,74.23; H,4.73; F,14.09; Si,6.94. Found C,74.15; H,4.77; F,12.85; Si,N/D. I.R. (nujol mull) ν_{max} 1600, 1570, 1480, 1400, 1255, 1105, 1000, 870, 760, 740, $680cm^{-1}$. ^1H n.m.r., $CDCl_3$, δ 2.9(s,2H), 6.8-7.4 (m,17H), ^{13}C n.m.r., $CDCl_3$, 22.921, 116.62, 117.5, 121.7, 122.6, 125, 128.3, 129, 129.7, 130.0, 131.4, 131.5, 135.9, 136.9, 157, 168.1 p.p.m. ^{29}Si n.m.r., $CDCl_3$, -12.2 p.p.m., d, J_{SiF} 3Hz. Mass spectrum M^+ 404.13, M^+-91 313.05.

Preparation of Phenyl(tris(m-fluorophenyl)silyl)(trimethylsilyl)-methane.- A 1.55M solution of butyllithium in hexane ($10cm^3$,16mmol) was added to benzyltri(m-fluorophenyl)silane (6g,15mmol) in hexamethylphosphoramide ($25cm^3$) and tetrahydrofuran ($25cm^3$) under nitrogen. To this was added chlorotrimethylsilane (1.5g,16mmol) and the reaction mixture heated for 5 minutes. The reaction was quenched with 2M hydrochloric acid ($5cm^3$), followed by addition of diethyl ether ($50cm^3$). The reaction mixture was washed with iced concentrated hydrochloric acid ($3x25cm^3$) and with saturated sodium hydrogen carbonate solution ($3x25cm^3$). The organic layer was dried over sodium sulphate and the solvent removed on a rotary evaporator. Recrystallization of the residue from hexane gave the product phenyl(tris(m-fluorophenyl)silyl)(trimethylsilyl)methane (2.3g,28%) m.p. 117-118°C, prisms,: Anal. Calcd for $Si_2C_{28}H_{27}F_3$: C,70.55; H,5.71; F,11.96; Si,11.79. Found C,70.44; H,5.77; F,11.2; Si,N/D. I.R. ν_{max}1570, 1480, 1410. 1255, 1100, 1035, 910, 780, 685cm^{-1}. ^1H n.m.r., $CDCl_3$, δ -0.13(s,9H), 2.5(s,1H), 6.8-7.3(m,17H), ^{13}C n.m.r., $CDCl_3$, 0.54, 26.9, 116.7, 117.7, 122.43, 123.3, 124.9, 128.8, 129.9, 130.2, 130.5, 132.1, 132.2, 138, 138.2, 140.2, 157.3, 168.3 p.p.m. ^{29}Si n.m.r., $CDCl_3$, 2.47, -13.04 p.p.m., d,J_{SiF}, 3Hz. Mass spectrum M^+476.13, M^+-15 461.1, M^+-92 384.09, M^+-163 313.05

Preparation of Phenyl(trimethylsilyl)(tris(p-methylphenyl)silyl)-methane.- Tri(p-methylphenyl)silane (25g,82mmol) was dissolved in ice cold carbon tetrachloride ($200cm^3$) and chlorine bubbled through the solution until the Si-H, ^1H n.m.r., signal disappeared. The solvent was removed on a rotary evaporator to give chlorotri(p-methylphenyl)silane (24g) which was used immediately at the next stage. A 1.55M solution of butyllithium in hexane ($40cm^3$,62mmol) was added to benzyltrimethylsilane (10g,60mmol) in tetramethylethylenediamine ($9cm^3$) and diethyl ether ($20cm^3$) under nitrogen. To this was added chlorotri(p-methylphenyl)silane (21g,63mmol) in tetrahydrofuran ($40cm^3$) and the reaction mixture was refluxed for 30 minutes. This was quenched with 2M hydrochloric acid ($5cm^3$) followed by washing with 2M hydrochloric acid ($2x10cm^3$) and then with saturated sodium hydrogen carbonate solution ($2x10cm^3$). The aqueous extracts were washed with diethyl ether ($20cm^3$) and ethereal extract combined with that of the reaction mixture. The ethereal solution was dried over sodium sulphate and the solvent removed on a rotary evaporator. The solid was recrystallized from hexane to give the product phenyl(trimethylsilyl)(tris(p-methylphenyl)silyl)methane (7.3g,26%) m.p. 130°C prisms: Anal. Calcd for $Si_2C_{31}H_{36}$: C,80.09; H,7.81; Si,12.1. Found C,80.14; H,7.86; Si N/D. I.R. (nujol mull) ν_{max} 1600, 1380, 1250, 1190, 1105, 910, 800, $700cm^{-1}$. ^1H n.m.r., $CDCl_3$, δ 0.0(s,9H), 2.51(s,9H), 2.68(s,1H), 7.2-7.6(m,17H). ^{13}C n.m.r., $CDCl_3$, 0.0, 21.34, 26.79, 123.63, 127.8, 128.23, 130.13, 132.35, 136.14, 138.75, 141.23 p.p.m. ^{29}Si n.m.r., $CDCl_3$, -13.34, 2.1 p.p.m. Mass spectrum M^+-15 449.22, M^+-73 391, M^+-163 301.1.

Preparation of Benzyltri(p-methoxyphenyl)silane.- Tri(p-methoxyphenyl)silane (40g,114mmol) and N-bromosuccinimide (20.1g,115mmol) in carbon tetrachloride (200cm^3) were heated until all the N-bromosuccinimide had reacted. The succinimide was filtered off and the solvent removed on a rotary evaporator to give the product bromotri(p-methoxyphenyl)silane (41g). Due to the reactive nature of this compound it was used immediately at the next stage. Benzyl chloride (12g,95mmol) was added to magnesium turnings (2.4g,100mmol) in tetrahydrofuran (100cm^3). After the Grignard reagent had been formed bromo-tri(p-methoxyphenyl)silane (41g,91mmol) in tetrahydrofuran (50cm^3) was added and the reaction mixture refluxed for 3 hours. The reaction mixture was quenched by saturated ammonium chloride (5cm^3), washed with water (100cm^3) and the solvent dried over sodium sulphate. The solvent was removed and recrystallization from ethanol gave the product benzyltri(p-methoxyphenyl)silane (14g,31%) m.p. 94-95°C,prisms: Anal. Calcd for Si $C_{28}H_{28}O_3$: C,76.31; H,6.41; Si,6.38;H,10.9. Found C,76.29; H,6.41; Si N/D; O,N/D. I.R.(nujol mull) ν_{max}1595, 1505, 1280, 1250, 1180, 1110, 1030, 815, 795cm^{-1}. ^{1}H n.m.r., $CDCl_3$, δ 2.83(s,2H), 3.8(s,9H), 6.8-7.33(m,17H), ^{13}C n.m.r., $CDCl_3$, 24.08, 54.92, 113.4, 124.26, 125.64, 127.9, 129, 136.9, 137.35, 136.68, 160.62 p.p.m. ^{29}Si n.m.r., $CDCl_3$, -12.84 p.p.m. Mass spectrum M^+440.31, M^+-91 349.18.

Preparation of Phenyl(tris(p-methoxyphenyl)silyl)(trimethylsilyl)-methane.- A 1.55M solution of n-butyllithium ($12cm^3$,19mmol) was added to benzyltri(p-methoxyphenyl)silane (7g,16mmol) in hexamethylphosphoramide ($25cm^3$) and tetrahydrofuran ($25cm^3$) under nitrogen. To this was added chlorotrimethylsilane (2.1g,20mmol) and the reaction mixture was warmed for 5 minutes. The reaction was quenched with 2M hydrochloric acid ($5cm^3$) followed by addition of diethyl ether ($50cm^3$). The organic layer was washed with iced concentrated hydrochloric acid ($3x25cm^3$) and then with saturated sodium hydrogen carbonate solution ($3x25cm^3$). The ethereal extracts were dried over sodium sulphate and the solvent removed on a rotary evaporator. Recrystallization from ethanol gave the product phenyl(tris(p-methoxyphenyl)silyl)(trimethylsilyl)methane (5.2g,63.4%) m.p. 114-115°C, prisms: Anal. Calcd for $Si_2C_{31}H_{36}O_3$: C,72.61; H,7.08; O,9.36; Si, 10.95. Found C,72.65; H,7.14; Si,N/D; O,N/D. I.R. (nujol mull) ν_{max}1590, 1505, 1375, 1280, 1250, 1180, 1110, 1025, 910, 700cm^{-1}. ^1H n.m.r., $CDCl_3$,δ -0.16(s,9H), 2.55(s,1H), 3.8(s,9H), 6.8-7.3(m,17H), ^{13}C n.m.r., $CDCl_3$, 0.23, 27.34, 54.92, 113.28, 123.8, 127.18, 128, 130.23, 137.7, 141.43, 160.4 p.p.m. ^{29}Si n.m.r., -13.63, 1.97 p.p.m. Mass spectrum M^+-15 497.19, M^+-163 349.11.

Preparation of Phenyl(trimethylsilyl)(triphenylsilyl)methane.- A 1.55M solution of butyllithium in hexane ($60cm^3$,90mmol) was added to benzyltrimethylsilane (15g,90mmol) in tetramethylethylenediamine ($12cm^3$) and diethyl ether ($20cm^3$) under nitrogen. To this was added chlorotriphenylsilane (26.5g,90mmol) dissolved in tetrahydrofuran ($40cm^3$) and the reaction mixture refluxed for 30 minutes. This was quenched with 2M hydrochloric acid ($5cm^3$) followed by washing with 2M hydrochloric acid ($2x10cm^3$) and then with saturated sodium hydrogen carbonate solution ($2x10cm^3$). The aqueous extracts were washed with diethyl ether ($20cm^3$) and ethereal extract combined with that of the reaction mixture. The ethereal extract was dried over sodium sulphate and the solvent removed on a rotary evaporator. The solid was recrystallized using hexane to give the product phenyl(trimethylsilyl)(triphenylsilyl)methane (18g,47%) m.p. 120-122°C, prisms: Anal. Calcd for $Si_2C_{28}H_{30}$: C,79.54; H,7.15; Si,13.3. Found C,79.47; H,6.95; Si,N/D. I.R. (nujol mull) ν_{max} 1590, 1425, 1375, 1245, 1200, 1100, 1020, 910, 800, 690cm^{-1}. ^1H n.m.r., $CDCl_3$, δ -0.12(s,9H), 2.59(s,1H), 7-7.5(m,20H), ^{13}C n.m.r., $CDCl_3$, 0.11. 26.7, 123, 127.53, 128, 129.2, 130.2, 135.7, 136.3, 141 p.p.m. ^{29}Si n.m.r., $CDCl_3$, -12.86, 2.33 p.p.m. Mass spectrum M^+422.19, M^+-15 407.16, M^+-73 349.14, M^+-163 259.06.

Preparation of Phenyl(t-butyldimethylsilyl)(trimethylsilyl)methane.- A 1.55M solution of butyllithium in hexane ($40cm^3$,62mmol) was added to benzyltrimethylsilane (10g,60mmol) in tetramethylethylenediamine ($9cm^3$) and diethyl ether ($20cm^3$) under nitrogen. To this was added t-butylchlorodiphenylsilane (9g,60mmol) and the reaction mixture refluxed for 10 minutes. This was quenched with 2M hydrochloric acid ($5cm^3$) followed by washing with 2M hydrochloric acid ($2x10cm^3$) and then with saturated sodium hydrogen carbonate solution ($2x10cm^3$). The aqueous extracts were washed with diethyl ether ($20cm^3$) and the ethereal extract combined with that of the reaction mixture. The ethereal solution was dried over sodium sulphate and the solvent removed on a rotary evaporator. The residue was distilled twice at reduced pressure to give the product phenyl(t-butyldimethylsilyl)-(trimethylsilyl)methane (6.1g,38%) b.p. 80-82°C (1mm Hg): Anal. Calcd. for $Si_2C_{16}H_{30}$: C,68.96; H, 10.86; Si, 20.18. Found C, 69.14; H, 10.88; Si, 20.17. I.R. (liquid film) νmax 2960, 2915, 2860, 1600, 1495, 1255, 1205, 1090, 910, 705cm^{-1}, ^1H n.m.r., $CDCl_3$, δ 0.03(s,9H), 0.14, 0.16(d,6H), 0.73(s,9H), 1.73(s,1H), 7-7.18(m,5H), ^{13}C n.m.r., $CDCl_3$,-3.95,-2.65, 0.87, 19.1, 26.2, 27.3, 123.6, 129.4, 143.9 p.p.m. ^{29}Si n.m.r., $CDCl_3$, 2.53, 6.2 p.p.m., Mass spectrum M^+ 278.19, M^+- 57 221.12.

2.3 Calibration of g.l.c. columns

Two g.l.c. columns were used in this study and were calibrated using prepared solutions of known quantities of cis or trans stilbenes and an internal standard (phenanthracene) in dichloromethane ($25cm^3$). The details of the calibration are shown in Tables 1A and 1B. Each peak ratio represents the average of 3 or 4 injections. The g.l.c. columns and conditions used were as follows.

Column 1; Packing 10% S.E.30 on chromosorb w 80-100 mesh, Length 2.7m, Internal Diameter 4mm, Carrier Gas (N_2) Flow Rate = $30cm^3/min$, Injector Temperature 300^oC, Column Temperature 225^oC, Detector Temperature 350^oC, Integrator Setting; Peak Width 24, Minimum Data 500, Threshold 100, Noise 10, Sampling 8, Attenuation 64×10^3.

Column 2; Packing 10% S.E.30 and 5% Apiezon (ratio 1:7) on chromosorb w 80-100 mesh, Length 2.7m, Internal Diameter 4mm, Carrier Gas (N_2) Flow Rate = $30cm^3/min$, Injector Temperature 300^oC, Column Temperature 225^oC, Detector Temperature 350^oC, Integrator Settings; Peak Width 24, Minimum Data 600, Threshold 100, Noise 10, Sampling 8, Attenuation 32×10^3.

Table 1A Calibration of the 10% SE.30 g.l.c. column.

	Solutions containing cis stilbene			Solutions containing trans stilbene		
Mass of stilbene W_1	0.0943g	0.2132g	0.1160g	0.1913g	0.098g	0.1059g
Mass of internal standard W_2	0.0917g	0.1023g	0.1992g	0.1053g	0.1117g	0.2023g
Mass Ratio W_1/W_2	1.034	2.017	0.582	1.845	0.877	0.523
Average Peak Ratio Stilbene/internal standard	1.094	2.158	0.610	1.914	0.876	0.517
Calibration Constant Peak ratio/Mass ratio	1.054	1.069	1.048	1.036	0.998	0.989

Average value for cis stilbene

Calibration constant = 1.0567 ± 0.01

Average value for trans stilbene

Calibration constant = 1.0066 ± 0.02

Table 1B Calibration of 10% S.E.30 and 5% Apiezon (ratio 1:7) g.l.c column

	Solutions containing cis stilbene			Solutions containing trans stilbene		
Mass of stilbene W_1	0.1016g	0.1753g	0.229g	0.2119g	0.138g	0.1269g
Mass of internal standard W_2	0.1313g	0.1428g	0.1228g	0.1247g	0.1939g	0.1013g
Mass Ratio = W_1/W_2	0.779	1.23	1.865	1.699	0.7117	1.253
Average Peak Ratio Stilbene/internal standard	0.791	1.273	1.909	1.764	0.734	1.302
Calibration Constant Peak ratio/Mass ratio	1.015	1.034	1.023	1.038	1.031	1.039

Average value for cis stilbene

Calibration constant = 1.024 ± 0.01

Average value for trans stilbene

Calibration constant = 1.036 ± 0.01

2.4. A General Method of determining the cis : trans stilbene ratio obtained from the Peterson Reaction

A typical procedure was as follows. Bis(trimethylsilyl)-phenylmethane (0.5g, 2mmol) was mixed with an excess of benzaldehyde (1.8g, 17mmol) in anhydrous hexamethylphosphoramide (25cm^3) in a nitrogen dry box at room temperature. To this was added an excess of sodium methoxide (0.2g, 4mmol). The reaction occurred rapidly and was quenched using iced concentrated hydrochloric acid (100cm^3). The mixture was extracted with dichloromethane (30-40cm^3) containing a known quantity of internal standard (0.15g). Each experiment was carried out twice and each solution being injected onto the g.l.c. twice. A sample calculation of yield and ratios of cis and trans stilbene is given below.

1st Experiment

Column used = 10% S.E.30

Mass of bis(trimethylsilyl)phenylmethane used = 0.5350g

Mass of internal standard used = 0.1807g

1st Injection

Mass of cis stilbene produced = 1.030/1.0567x0.1807 = 0.1761g.

Mass of trans stilbene produced = 1.264/1.0066x0.1807 = 0.2269g.

Total mass of stilbene = 0.403g. Mass of stilbene expected = 0.4083g.

% Yield = 98.7%. Ratio cis:trans = 1:1.29.

2nd Injection

Mass of cis stilbene produced = 1.029/1.0567x0.1807 = 0.1759g.

Mass of trans stilbene produced = 1.266/1.0066x0.1807 = 0.2273g.

Total mass of stilbene = 0.4032g. Mass of stilbene expected = 0.4083g.

% Yield = 98.8%. Ratio cis:trans = 1:1.29.

2nd Experiment

Mass of bis(trimethylsilyl)phenylmethane used = 0.5350g.

Mass of internal standard used = 0.1587g.

1st Injection

Mass of cis stilbene produced = 1.048/1.0567x0.1587 = 0.1574g.

Mass of trans stilbene produced = 1.335/1.0066x0.1587 = 0.2104g.

Total mass of stilbene = 0.3678g. Mass of stilbene expected = 0.3765g.

% Yield = 97.7%. Ratio cis:trans = 1:1.33.

2nd Injection

Mass of cis stilbene produced = 1.066/1.0567x0.1587 = 0.1601g.

Mass of trans stilbene produced = 1.340/1.0066x0.1587 = 0.2112g.

Total mass of stilbene = 0.3713g. Mass of stilbene expected = 0.3765g.

% Yield = 98.6%. Ratio cis:trans = 1:1.32.

2.5. An Investigation of the possible Isomerization of Stilbene Products

A known quantity of cis or trans stilbene was added to the reaction mixture before the addition of sodium methoxide. The reaction was carried out as in section 2.4 and the quantities of cis and trans stilbene present were determined. By subtracting the quantity of added cis or trans stilbene it was possible to determine the cis:trans ratio of the products of the reaction. The results are shown in Table 2. The constancy of the cis:trans ratio, irrespective of the amount of added cis or trans stilbenes indicates that the cis and trans stilbenes retain their structural integrity during the reaction.

2.6. The Effect of varying the alkoxide salt used to generate the α-silylbenzyl carbanion

The following reactions were performed as in section 2.4 but using different alkoxides to generate the α-silylbenzyl carbanion. The alkoxides employed were potassium tert-butoxide (0.2g), lithium tert-butoxide (0.18g), sodium n-propoxide (0.25g) and sodium silanolate (0.35g). The results are shown on Table 3.

2.7. The Effect of Temperature on the Peterson Reaction

A series of reactions were performed as described in section 2.4 but at different temperatures. The reactions were left to stand for no longer than one minute to avoid the possibility of isomerization of the cis or trans stilbene. The results are given in Table 4.

Table 2 An Investigation of the possible Isomerization of Stilbene Products

	Addition of *cis* stilbene		Addition of *trans* stilbene	
Mass of bis(trimethylsilyl)phenylmethane used	0.5999g	0.6604g	0.4498g	0.5343g
Mass of internal standard used	0.174g	0.1789g	0.1462g	0.1675g
Mass of stilbene added	0.1081g	0.2310g	0.0477g	0.0781g
Mass of *cis* stilbene present determined by g.l.c. a	0.3070g	0.4555g	0.1482g	0.1735
Mass of *trans* stilbene present determined by g.l.c. a	0.2625g	0.2980g	0.2437g	0.3127g
Cis:*Trans* ratio after correction for added stilbene	1:1.32	1:1.33	1:1.32	1:1.35
% Yield after correction for added stilbene	101%	103%	100%	100%

a = Average of 2 injections $\pm$ 0.001g

Volume of hexamethylphosphoramide used = $25cm^3$

Mass of benzaldehyde used = 1.8g

Mass of sodium methoxide used = 0.2g

Table 3 The Results of Peterson Reactions carried out using different alkoxide salts to generate the α-silylbenzyl carbanion

g.l.c. Column used = 10% S.E.30

	KO^tBu	KO^tBu	NaO^nPr	NaO^nPr	$NaOSiMe_3$	$NaOSiMe_3$	LiO^tBu	LiO^tBu
Mass of bis(trimethylsilyl)-phenylmethane used	0.5356g	0.4335g	0.4856g	0.4291g	0.6111g	0.5906g	0.4505g	0.4009g
Mass of internal standard used	0.1626g	0.1467g	0.1639g	0.1595g	0.1567g	0.1505g	0.1579g	0.1759g
Mass of cis stilbene produced a	0.1805g	0.1449g	0.1440g	0.1366g	0.2036g	0.1990g	0.1431g	0.1251g
Mass of trans stilbene produced a	0.2326g	0.1833g	0.2065g	0.1845g	0.2636g	0.2494g	0.2029g	0.1803g
Yield of stilbene	0.4131g	0.3292g	0.3505g	0.3211g	0.4772g	0.4484g	0.3460g	0.3054g
Expected yield of stilbene	0.4088g	0.3308g	0.3706g	0.3275g	0.4664g	0.4507g	0.3438g	0.3060g
% Yield of Reaction	101%	99%	97%	98%	100%	99%	101%	100%
Ratio of cis:trans stilbenes	1:1.29	1:1.27	1:1.33	1:1.34	1:1.30	1:1.29	1:1.42	1:1.44

a = Average of 2 injections $\pm$ 0.001g

Volume of hexamethylphosphoramide used = $25cm^3$

Mass of benzaldehyde used = 0.9g

Table 4

The Results of Peterson Reactions performed at different Temperatures

g.l.c. Column used = 10% S.E.30

	5°C	5°C	24-26°C	25-27°C	43-47°C	45-50°C	75-78°C	75-79°C
Mass of bis(trimethylsilyl)-phenylmethane used	0.5403g	0.4704g	0.4803g	0.4395g	0.4526g	0.5258g	0.3613g	0.5273g
Mass of internal standard used	0.1655g	0.1894g	0.1582g	0.1588g	0.1688g	0.1749g	0.1412g	0.1811g
Mass of cis stilbene produced a	0.1776g	0.1562g	0.1549g	0.1451g	0.1449g	0.1813g	0.1136g	0.170g
Mass of trans stilbene produced a	0.2236g	0.1955g	0.2041g	0.1910g	0.1907g	0.2234g	0.1583g	0.2342g
Yield of stilbene	0.3912g	0.3517g	0.3590g	0.3361g	0.3456g	0.4047g	0.2719g	0.4042g
Expected yield of stilbene	0.4124g	0.3590g	0.3666g	0.3354g	0.3454g	0.4013g	0.2757g	0.4024g
% Yield of Reaction	97%	98%	98%	100%	97%	98%	99%	100%
Ratio of cis:trans stilbene	1:1.26	1:1.25	1:1.32	1:1.32	1:1.31	1:1.35	1:1.39	1:1.37

a = Average value of 2 injections $\pm$ 0.001g

Volume of hexamethylphosphoramide used = 25cm^3

Mass of benzaldehyde used = 0.9g

Mass of sodium methoxide used = 0.2g

2.8 Effect of adding inorganic salts to the Peterson Reaction

The following reactions were performed in the presence of various inert ionic salts. A typical procedure is given below.

A known weight of lithium iodide was added to hexamethylphosphoramide ($25cm^3$) containing bis(trimethylsilyl)phenylmethane (0.5g,4mmol) and benzaldehyde (1.8g,17mmol). To this solution was added sodium methoxide (0.2g,4mmol) and the reaction was worked up as in section 2.4. The results are shown in Table 5. The Peterson Reaction was also performed in the presence of sodium tetraphenylboron using the same quantities of solvent and reactants as given above. These results are shown in Table 6. Finally the reaction was carried out in the presence of lithium perchlorate. The α-silylbenzyl carbanion was generated using lithium tert-butoxide (0.2g,3mmol) and the conditions of the reactions were as above. The results are shown in Table 7.

2.9 Effect of solvent on the Peterson Reaction

The reactions were performed in a range of solvents. The solvents employed were dimethylformamide, dimethylsulphoxide and tetrahydrofuran/hexamethylphosphoramide mixtures. The α-silylbenzyl carbanions were generated using a range of alkoxides and the reactions were performed as described in section 2.4. The results are given in Tables 8 - 12.

The reaction was also performed in tetrahydrofuran in the presence of crown ethers. A typical procedure was as follows.

Bis(trimethylsilyl)phenylmethane (0.5g,2mmol), benzaldehyde (0.9g,8mmol) and 18-crown-6 ether (0.7g,2.5mmol) were mixed together

in anhydrous tetrahydrofuran ($25cm^3$). To this mixture was added potassium methoxide (0.15g,3mmol) and the reaction quenched by addition of iced hydrochloric acid ($100cm^3$). The reaction was then extracted with diethyl ether ($20cm^3$) containing a known quantity of internal standard. The results are given on Table 13.

2.10 An Investigation of the Effect of Magnesium Iodide on the Peterson Reaction

A Peterson Reaction was performed in the presence of magnesium iodide (0.8g,7mmol) as described in section 2.6 but using sodium silanolate (0.35g,3.5mmol) to generate the α-silylbenzyl carbanion.

A series of reactions were also performed in which the benzyltrimethylsilyl anion was prepared and then quenched by the addition of benzaldehyde. A typical procedure was as follows.

To bis(trimethylsilyl)phenylmethane (0.7g,3mmol) in hexamethylphosphoramide ($25cm^3$) was added sodium silanolate (0.35g,3.5mmol), to give the red coloured anion solution. This was quenched by the addition of benzaldehyde (0.9g,8mmol) and the reaction mixture was worked up as described in section 2.2. This reaction was repeated except that magnesium iodide (0.8g,7mmol) was added to the benzyltrimethylsilyl anion solution prior to addition of benzaldehyde. The results are given on Table 14.

Table 5

The effect of addition of Lithium Iodide to the Peterson Reaction

Alkoxide used = sodium methoxide (0.2g)

g.l.c. column used = 10% S.E.30

	Mass of Lithium Iodide added					
	0.1g	0.1g	0.3g	0.3g	0.9g	0.9g
Mass of bis(trimethylsilyl)phenylmethane used	0.5051g	0.5510g	0.4803g	0.4643g	0.3993g	0.4473g
Mass of internal standard used	0.1627g	0.1603g	0.1543g	0.1725g	0.1629g	0.1762g
Mass of cis stilbene produced a	0.1777g	0.1821g	0.1087g	0.1039g	0.0059g	0.0083g
Mass of trans stilbene produced a	0.2326g	0.2412g	0.1675g	0.1452g	0.073g	0.086g
Yield of stilbenes	0.4103g	0.4233g	0.2762g	0.2491g	0.0789g	0.0943g
Expected yield of stilbenes	0.386g	0.4205g	0.3665g	0.3543g	0.3047g	0.341
% Yield of reaction	106%	100%	75%	70%	26%	27%
Ratio of cis:trans stilbene	1:1.31	1:1.31	1:1.54	1:1.37	1:12.2	1:10.6

a = Average value of 2 injections $\pm$ 0.001g

Solvent used = hexamethylphosphoramide ($25cm^3$)

Mass of benzaldehyde used = 1.8g

Table 6

The Effect of addition of sodium tetraphenylboron to the Peterson Reaction

Alkoxide used = sodium methoxide (0.2g)

g.l.c. column used = 10% S.E.30

	Mass of sodium tetraphenylboron added					
	0.2g	0.2g	0.6g	0.6g	1.2g	1.2g
Mass of bis(trimethylsilyl)phenylmethane used	0.4657g	0.4489g	0.4762g	0.4666g	0.4786g	0.4922g
Mass of internal standard used	0.1580g	0.1658g	0.1797g	0.1652g	0.1649g	0.1793g
Mass of cis stilbene produced a	0.1516g	0.1492g	0.1468g	0.1465g	0.1704g	0.1740g
Mass of trans stilbene produced a	0.1827g	0.1745g	0.1717g	0.1692g	0.1959g	0.1901g
Yield of stilbenes	0.3343g	0.3237g	0.3185g	0.3157g	0.3763g	0.3641g
Expected yield of stilbenes	0.3554g	0.3425g	0.3634g	0.3561g	0.3625g	0.3756
% Yield of reaction	94%	94%	88%	89%	101%	95%
Ratio of cis:trans stilbenes	1:1.21	1:1.19	1:1.17	1:1.15	1:1.15	1:1.10

a = Average value of 2 injections $\pm$ 0.001g

Volume of hexamethylphosphoramide used = 25cm^3

Mass of benzaldehyde used = 1.8g

Table 7

The effect of addition of lithium perchlorate to the Peterson Reaction

Alkoxide used = lithium tert-butoxide (0.2g)

g.l.c. column used = 10% S.E.30

	Mass of lithium perchlorate added					
	0.2g	0.2g	0.4g	0.4g	0.8g	0.8g
Mass of bis(trimethylsilyl)phenylmethane used	0.4506g	0.5246g	0.4134g	0.4807g	0.4127g	0.4787g
Mass of internal standard used	0.1677g	0.1598g	0.1719g	0.161g	0.170g	0.1637g
Mass of cis stilbene produced a	0.1243g	0.1525g	0.0882g	0.1103g	0.0729g	0.073g
Mass of trans stilbene produced a	0.1787g	0.2158g	0.1307g	0.1575g	0.1097g	0.1056g
Yield of stilbenes	0.3030g	0.3683g	0.2189g	0.2678g	0.1826g	0.1786g
Expected yield of stilbenes	0.3437g	0.4004g	0.3155g	0.3669g	0.3149g	0.3653g
% Yield of reaction	88%	92%	69%	73%	57%	49%
Ratio of cis:trans stilbene	1:1.43	1:1.42	1:1.48	1:1.43	1:1.50	1:1.45

a = Average value of 2 injections ± 0.001g

Volume of hexamethylphosphoramide used = $25cm^3$

Mass of benzaldehyde used = 1.8g

Table 8 The result of Peterson Reaction performed in tetrahydrofuran/hexamethylphosphoramide solvent system

Alkoxide used = Lithium tert-butoxide (0.2g)

g.l.c. column used = 10% S.E.30

	% Tetrahydrofuran in solvent mix			
	20%	20%	40%	40%
Mass of bis(trimethylsilyl)phenylmethane used	0.5329g	0.4704g	0.5573g	0.5775g
Mass of internal standard used	0.1861g	0.1603g	0.1651g	0.1670g
Mass of cis stilbene produced a	0.1714g	0.1513g	0.1087g	0.1055g
Mass of trans stilbene produced a	0.2284g	0.2004g	0.1558g	0.1380g
Yield of stilbenes	0.3998g	0.3537g	0.2635g	0.2435g
Expected yield of stilbenes	0.4078g	0.3611g	0.4543g	0.4198g
% Yield of reaction	98%	98%	58%	58%
Ratio of cis:trans stilbenes	1:1.33	1:1.32	1:1.25	1:1.30

a = Average value of 2 injections $\pm$ 0.001g

Total volume of solvent = $25cm^3$

Mass of benzaldehyde used = 0.9g

Table 9 The Results of Peterson Reaction performed in tetrahydrofuran/hexamethylphosphoramide solvent

Alkoxide used = sodium methoxide (0.2g)

g.l.c. column used = 10% S.E.30

	% Tetrahydrofuran in solvent mix							
	20%	20%	40%	40%	50%	50%	70%	70%
Mass of bis(trimethylsilyl)-phenylmethane used	0.4124g	0.540g	0.5068g	0.5252g	0.5859g	0.5549g	0.5045g	0.5526g
Mass of internal standard used	0.1825g	0.1837g	0.1851g	0.1912g	0.1719g	0.1917g	0.1596g	0.1922g
Mass of cis stilbene produced a	0.1377g	0.1887g	0.1584g	0.170g	0.1775g	0.1667g	0.1091g	0.1171g
Mass of trans stilbene produced a	0.1786g	0.2515g	0.2196g	0.2288g	0.2618g	0.2492g	0.1652g	0.1797g
Yield of stilbenes	0.3163g	0.4402	0.3780g	0.3988g	0.4393	0.4159g	0.2743g	0.2968g
Expected yield of stilbenes	0.3147g	0.4121g	0.387g	0.4008g	0.4472g	0.4235g	0.3850g	0.4217g
% Yield of reaction	100%	107%	98%	99%	98%	98%	71%	70%
Ratio of cis:trans stilbenes	1:1.29	1:1.31	1:1.39	1:1.34	1:1.47	1:1.49	1:1.51	1:1.53

a = Average value of 2 injections $\pm$ 0.001g

Total volume of solvent = 25cm^3

Mass of benzaldehyde used = 0.9g

Table 10 The Results of Peterson Reaction performed in tetrahydrofuran/hexamethylphosphoramide solvent system

Alkoxide used = potassium tert-butoxide (0.2g)

g.l.c. column used = 10% S.E.30

	% Tetrahydrofuran in solvent mix							
	20%	20%	40%	40%	60%	60%	80%	80%
Mass of bis(trimethylsilyl)-phenylmethane used	0.4212g	0.4345g	0.5083g	0.4678g	0.443g	0.4225g	0.4376g	0.4662g
Mass of internal standard used	0.1416g	0.1485g	0.1503g	0.1516g	0.1569g	0.1447g	0.1575g	0.1422g
Mass of cis stilbene produced a	0.1351g	0.1416g	0.1663g	0.1491g	0.1458g	0.1364g	0.1373g	0.1479g
Mass of trans stilbene produced a	0.1790g	0.1835g	0.2175g	0.1973g	0.1861g	0.1767g	0.1849g	0.1946g
Yield of stilbenes	0.3141g	0.3251g	0.3838g	0.3464g	0.3319g	0.3131g	0.3222g	0.3425g
Expected yield of stilbenes	0.3216g	0.3315g	0.3879g	0.3570g	0.3381g	0.3224g	0.3339g	0.3558g
% Yield of reaction	98%	98%	99%	97%	98%	97%	96%	96%
Ratio of cis:trans stilbenes	1:1.32	1:1.30	1:1.31	1:1.33	1:1.28	1:1.30	1:1.34	1:1.32

a = Average value of 2 injections $\pm$ 0.001g

G Total volume of solvent = 25cm^3

Mass of benzaldehyde used = 0.9g

Table 11

The Results of Peterson Reaction carried out in Dimethylformamide

g.l.c. column used = 10% S.E.30

	Alkoxide used				
	$NaOSiMe_3$	$NaOSiMe_3$	$NaOSiMe_3$	NaO^nPr	NaO^nPr
Mass of bis(trimethylsilyl)phenylmethane used	0.5115g	0.4978g	0.6146g	0.4996g	0.5586g
Mass of internal standard used	0.1620g	0.165g	0.1813g	0.1710g	0.1662g
Mass of alkoxide used	0.2g	0.3g	0.4g	0.2g	0.3g
Mass of benzaldehyde used	0.9g	2.7g	0.9g	0.9g	2.7g
Volume of dimethylformamide used	$30cm^3$	$35cm^3$	$35cm^3$	$30cm^3$	$35cm^3$
Mass of cis stilbene produced a	0.0661g	0.1590g	0.2102g	0.1093g	0.1758g
Mass of trans stilbene produced a	0.0732g	0.1767g	0.2409g	0.1199g	0.1984g
Yield of stilbenes	0.1393g	0.3357g	0.4511g	0.2292g	0.3742g
Expected yield of stilbenes	0.3904g	0.3794g	0.4691g	0.3813g	0.4263g
% Yield of reaction	36%	89%	96%	60%	88%
Ratio of cis:trans stilbenes	1:1.10	1:1.11	1:1.14	1:1.07	1:1.13

a = Average value of 2 injections $\pm$ 0.001g

Table 12

The Results of Peterson Reaction carried out in Dimethylsulphoxide

g.l.c. column used = 10% S.E.30

Volume of DMSO used = $30cm^3$

	Alkoxide used			
	$NaOSiMe_3$ [b]	$NaOSiMe_3$ [b]	KO^tBu [c]	KO^tBu [c]
Mass of bis(trimethylsilyl)phenylmethane used	0.5647g	0.5307g	0.4512g	0.5107g
Mass of internal standard used	0.1992g	0.1528g	0.1632g	0.1535g
Mass of cis stilbene produced a	0.1872g	0.1908g	0.1454g	0.1607g
Mass of trans stilbene produced a	0.2254g	0.2258g	0.1909g	0.2098g
Yield of stilbenes	0.4126g	0.4266g	0.3363g	0.3705g
Expected yield of stilbenes	0.4310g	0.405g	0.3444g	0.3828g
% Yield of reaction	96%	103%	97%	97%
Ratio of cis:trans stilbenes	1:1.21	1:1.19	1:1.32	1:1.30

a = Average value of 2 injections $\pm$ 0.001g

b = Mass of sodium silanolate used = 0.4g Mass of benzaldehyde used = 0.9g

c = Mass of potassium tert-butoxide used = 0.2g Mass of benzaldehyde used = 1.4g

Table 13 The Results of Peterson Reaction performed in neat Tetrahydrofuran and in the presence of Crown Ethers

g.l.c. column used = 10% S.E.30

	Neat THF b	THF + 18-Crown-6 c	Ether b	THF + Dibenzo-18-Crown-6 c	Ether c
Mass of bis(trimethylsilyl)phenylmethane used	0.4052g	0.4874g	0.6245g	0.4607g	0.4673g
Mass of internal standard used	0.1568g	0.1685g	0.1678g	0.1730g	0.1643g
Mass of crown ether used	-	0.7g	0.7g	0.9g	0.9g
Mass of cis stilbene produced a	0.0597g	0.1342g	0.1711g	0.0496g	0.0557g
Mass of trans stilbene produced a	0.0330g	0.1932g	0.2454g	0.0571g	0.0597g
Yield of stilbenes	0.0927g	0.3274g	0.4165g	0.1067g	0.1054g
Expected yield of stilbenes	0.3092g	0.3720g	0.4766g	0.3504g	0.3566g
% Yield of reaction	30%	88%	87%	35%	22%
Ratio of cis:trans stilbenes	1:0.55	1:1.44	1:1.43	1:1.15	1:1.07

a = Average value of 2 injections ± 0.001g

b = Mass of potassium tert-butoxide used = 0.2g

c = Mass of potassium methoxide used = 0.15g

Mass of benzaldehyde used in each experiment = 0.9g

Volume of tetrahydrofuran used in each experiment = 25cm^3

Table 14

The Effect of Magnesium Iodide on the Peterson Reaction

g.l.c. column used = 5% Apiezon
10% S.E.30 (ratio 7:1)

	MgI_2 added to Peterson Reaction		$NaOSiMe_3$	$NaOSiMe_3/MgI_2$	
				b^1	b^2
Mass of bis(trimethylsilyl)phenylmethane used	0.6555g	0.6193g	0.6816g	0.7525g	0.8036g
Mass of internal standard used	0.1004g	0.1074g	0.1380g	0.1336g	0.1169g
Mass of <u>cis</u> stilbene produced a	0.0904g	0.0595g	0.1260g	0.0396g	0.1211g
Mass of <u>trans</u> stilbene produced a	0.1632g	0.0972g	0.1551g	0.0710g	0.2365g
Yield of stilbenes	0.2536g	0.1567g	0.2811g	0.1106g	0.3576g
Expected yield of stilbenes	0.4503g	0.4726g	0.5202g	0.5743g	0.6133g
% Yield of reaction	56%	33%	54%	19%	57%
Ratio of <u>cis</u>:<u>trans</u> stilbenes	1:1.81	1:1.63	1:1.24	1:1.76	1:1.96

a = Average value of 2 injections $\pm$ 0.001g

b^1 = Quenched after 15 minutes

b^2 = Quenched after 2 minutes

Volume of hexamethylphosphoramide used = $25cm^3$

Mass of benzaldehyde used = 0.9g

Mass of magnesium iodide used = 0.8g

2.11 An Investigation of Reaction between trimethylsilyl sodium and trans stilbene oxide.

Hexamethyldisilane (0.5g,3mmol) and trans stilbene oxide (0.55g,3mmol) were mixed together in hexamethylphosphoramide ($25cm^3$). To this was added sodium methoxide (0.15g,3mmol), the solution turned a dark red colour and was left to stand at room temperature for 30 minutes. The reaction was quenched by adding iced concentrated hydrochloric acid ($100cm^3$) and extracted with dichloromethane ($30cm^3$). Analysis of this extraction by gas chromatographic mass spectrometry showed the major products were bibenzyl and 1-trimethylsilyl-1,2-diphenylethane.

2.12 The effect of varying the substituent groups on Silicon on the cis:trans ratio of stilbenes produced by the Peterson Reaction

The α,α-bissilyl toluenes described in section 2.2 were prepared and reacted as described in section 2.4. In these compounds the groups attached to one of the silicon atoms were sterically large (eg ^{t}butyldimethyl) and this should hinder attack of the alkoxide at this site. This hypothesis was confirmed by adding sodium methoxide to the bissilyl toluene in hexamethylphosphoramide and quenching the resulting anion by the addition of 2M hydrochloric acid. Examination of the products by g.l.c. showed that the silicon containing the sterically large groups was retained and the trimethylsilyl group had been eliminated. A typical procedure was as follows.

To phenyl(t-butyldimethylsilyl)(trimethylsilyl)methane (0.9g, 3mmol) in hexamethylphosphoramide ($25cm^3$) was added sodium methoxide (0.2g,3.5mmol). The dark red solution was quenched with 2M hydrochloric acid ($50cm^3$) and extracted with chloroform.

Examination of the chloroform extract by g.l.c. showed the presence of only the t-butyldimethylsilyl toluene.

With phenyl(dimethylphenylsilyl)(trimethylsilyl)methane attack occurred at both silicon groups thus in this case bis(dimethylphenylsilyl)phenylmethane was employed.

The results of the Peterson reactions performed using these substituents are given in Tables 15-27.

Table 15

The Results of the Peterson Reaction performed using Phenyl(triethylsilyl)-(trimethylsilyl)methane

Column used = 10% S.E.30

	Alkoxide used			
	$NaOSiMe_3$[c]	$NaOSiMe_3$[c]	KO^tBu[b]	KO^tBu[b]
Mass of Phenyl(triethylsilyl)(trimethylsilyl)methane used	0.4781g	0.4937g	0.4769g	0.5644g
Mass of internal standard used	0.1394g	0.1476g	0.1602g	0.1518g
Mass of cis stilbene produced a	0.1382g	0.1418g	0.1326g	0.1560g
Mass of trans stilbene produced a	0.1701g	0.1771g	0.1634g	0.1996g
Yield of stilbenes	0.3083g	0.3189g	0.2960g	0.3556g
Expected yield of stilbenes	0.3102g	0.3199g	0.3032g	0.3657g
% Yield of reaction	99%	100%	98%	98%
Ratio of cis:trans stilbenes	1:1.23	1:1.25	1:1.24	1:1.28

a = Average value of 2 injections $\pm$ 0.001g

b = Mass of potassium t-butoxide used = 0.2g

c = Mass of sodium silanolate = 0.25g

Volume of hexamethylphosphoramide used = $25cm^3$

Mass of benzaldehyde used = 0.9g

Table 16

The results of the Peterson Reaction performed using Phenyl(diisobutylmethylsilyl)(trimethylsilyl)methane

Column used = 5% Apiezon, 10% S.E.30 ratio (7:1)

	Alkoxide used	
	$NaOSiMe_3$	$NaOSiMe_3$
Mass of phenyl(diisobutylmethylsilyl)(trimethylsilyl)methane used	0.5442g	0.4404g
Mass of internal standard used	0.1583g	0.1324g
Mass of cis stilbene produced a	0.1325g	0.1067
Mass of trans stilbene produced a	0.1539g	0.1230g
Yield of stilbenes	0.2864g	0.2297
Expected yield of stilbenes	0.3060g	0.2476g
% Yield of reaction	94%	93%
Ratio of cis:trans stilbene produced	1:1.16	1:1.15

a = Average value of 2 injections $\pm$ 0.001g

Volume of hexamethylphosphoramide used = $25cm^3$

Mass of benzaldehyde used = 1.8g

Mass of sodium silanolate used = 0.25g

Table 17

The results of the Peterson Reaction performed using

Phenyl(dicyclohexylmethylsilyl)(trimethylsilyl)methane

Column used = 5% Apiezon, 10% S.E.30 ratio (7:1)

	Alkoxide used	
	$NaOSiMe_3$	$NaOSiMe_3$
Mass of phenyl(dicyclohexylmethylsilyl)(trimethylsilyl)methane used	0.5083g	0.5652g
Mass of internal standard used	0.1630g	0.1495g
Mass of *cis* stilbene produced a	0.1073g	0.1181g
Mass of *trans* stilbene produced a	0.1209g	0.1369g
Yield of stilbenes	0.2282g	0.2550g
Expected yield of stilbenes	0.2460g	0.2734g
% Yield of reaction	93%	93%
Ratio of *cis*:*trans* stilbene	1:1.13	1:1.15

a = Average value of 2 injections $\pm$ 0.001g

Volume of hexamethylphosphoramide used = $25cm^3$

Mass of benzaldehyde used = 0.9g

Mass of sodium silanolate used = 0.25g

Table 18

The results of the Peterson Reaction performed using Phenyl(t-butyldimethylsilyl)(trimethylsilyl)methane

Column ysed = 5% Apiezon, 10% S.E.30 ratio (7:1)

	Alkoxide used					
	LiO^tBu	LiO^tBu	NaOMe	NaOMe	KO^tBu	KO^tBu
Mass of phenyl(t-butyldimethylsilyl)-(trimethylsilyl)methane used	0.6121g	0.5407g	0.5628g	0.5312g	0.6061g	0.4845g
Mass of internal standard used	0.1607g	0.1807g	0.1592g	0.1659g	0.1665g	0.1754g
Mass of cis stilbene produced a	0.1908g	0.1709g	0.1727g	0.1641g	0.1816g	0.1491g
Mass of trans stilbene produced a	0.2132g	0.1887g	0.1800g	0.1689g	0.2059g	0.1658g
Yield of stilbenes	0.4040g	0.3596g	0.3527g	0.3330g	0.3875g	0.3149
Expected yield of stilbenes	0.3966g	0.3504g	0.3647	0.3342g	0.3927g	0.3139
% Yield of reaction	101%	102%	97%	100%	98%	100%
Ratio of cis:trans stilbene	1:1.11	1:1.10	1:1.04	1:1.03	1:1.13	1:1.11

a = Average value of 2 injections $\pm$ 0.001g

Volume of hexamethylphosphoramide used = $25cm^3$

Mass of benzaldehyde used = 0.9g

Mass of alkoxide used in each case = 0.2g

Table 19

The results of the Peterson Reaction performed using Phenyl(dimethylphenylsilyl)(trimethylsilyl)methane

Column used = 10% S.E.30

	Alkoxide used			
	NaOMe	NaOMe	KO^{t}Bu	KO^{t}Bu
Mass of phenyl(dimethylphenylsilyl)(trimethylsilyl)methane used	0.528g	0.6256g	0.5762g	0.5596g
Mass of internal standard used	0.1674g	0.1586g	0.1531g	0.1769g
Mass of cis stilbene produced a	0.1397g	0.1672g	0.1459g	0.1451g
Mass of trans stilbene produced a	0.1773g	0.2129g	0.1907g	0.1854g
Yield of stilbenes	0.3170g	0.3801g	0.3466g	0.3305g
Expected yield of stilbenes	0.3189g	0.3780g	0.3480g	0.3380g
% Yield of reaction	100%	100%	96%	97%
Ratio of cis:trans stilbene	1:1.27	1:1.27	1:1.31	1:1.28

a = Average value of 2 injections $\pm$ 0.001g

Volume of hexamethylphosphoramide used = 25cm^3

Mass of benzaldehyde used = 0.9g

Mass of alkoxide used in each case = 0.2g

Table 20

The results of the Peterson Reaction performed using Bis(dimethylphenylsilyl)phenylmethane

Column used = 10% S.E.30

	Alkoxide used	
	KO^tBu	KO^tBu
Mass of bis(dimethylphenylsilyl)phenylmethane used	0.6714g	0.5625g
Mass of internal standard used	0.1436g	0.1501g
Mass of cis stilbene produced a	0.1450g	0.1176g
Mass of trans stilbene produced a	0.18790g	0.1563g
Yield of stilbenes	0.3240g	0.2739g
Expected yield of stilbenes	0.3360	0.2815
% Yield of reaction	96%	97%
Ratio of cis:trans stilbene	1:1.25	1:1.32

a = Average value of 2 injections ± 0.001g

Volume of hexamethylphosphoramide used = $25cm^3$

Mass of benzaldehyde used = 0.9g

Mass of potassium t-butoxide = 0.2g

Table 21

The results of the Peterson Reaction performed using Phenyl(methyldiphenylsilyl)(trimethylsilyl)methane

Column used = 10% S.E.30

	Alkoxide used	
	$NaOSiMe_3$	$NaOSiMe_3$
Mass of phenyl(methyldiphenylsilyl)(trimethylsilyl)methane used	0.5762g	0.5783g
Mass of internal standard used	0.1519g	0.1145g
Mass of cis stilbene produced a	0.1187g	0.1211g
Mass of trans stilbene produced a	0.1748g	0.1630g
Yield of stilbenes	0.2935g	0.2841g
Expected yield of stilbenes	0.2883g	0.2894g
% Yield of reaction	101%	98%
Ratio of cis:trans stilbene	1:1.47	1:1.35

a = Average value of 2 injections $\pm$ 0.001g

Volume of hexamethylphosphoramide used = $25cm^3$

Mass of benzaldehyde used = 0.9g

Mass of sodium silanolate used = 0.25g

Table 22

The results of the Peterson Reaction performed using Phenyl(t-butyldiphenylsilyl)(trimethylsilyl)methane

Column used = 10% S.E.30

	Alkoxide used						
	LiO^tBu	$NaOSiMe_3$	$NaOSiMe_3$	NaOMe	NaOMe	KO^tBu	KO^tBu
Mass of phenyl(t-butyldiphenylsilyl)-(trimethylsilyl)methane used	0.7318g	0.5731g	0.5274g	0.6232g	0.6007g	0.6477g	0.5596g
Mass of internal standard used	0.1605g	0.1479g	0.1637g	0.1373g	0.133g	0.1631g	0.1498g
Mass of alkoxide used	0.4g	0.35g	0.35g	0.2g	0.2g	0.4g	0.4g
Mass of cis stilbene produced a	0.0679g	0.1543g	0.1319	0.1667g	0.1519g	0.1601g	0.1349g
Mass of trans stilbene produced a	0.048g	0.0993g	0.0871g	0.1055g	0.1042g	0.1187g	0.1030g
Yield of stilbenes	0.1159g	0.2536g	0.2190g	0.2722	0.2561g	0.2788g	0.2379g
Expected yield of stilbenes	0.328g	0.2569g	0.2364g	0.2793	0.2692g	0.2903g	0.2508g
% Yield of reaction	35%	99%	94%	97%	95%	96%	96%
Ratio of cis:trans stilbene	1:0.71	1:0.64	1:0.66	1:0.63	1:0.69	1:0.74	1:0.76

a = Average value of 2 injections $\pm$ 0.001g

Volume of hexamethylphosphoramide used = $30cm^3$

Mass of benzaldehyde used = 0.9g

Table 23

The results of the Peterson Reaction performed using Phenyl(tris(p-methoxyphenyl)silyl)(trimethylsilyl)methane

Column used = 10% S.E.30

	Alkoxide used			
	$NaOSiMe_3$	$NaOSiMe_3$	KO^tBu	KO^tBu
Mass of phenyl(tris(p-methoxyphenyl)silyl)(trimethylsilyl)-methane used	0.5848g	0.6553g	0.5450g	0.5742g
Mass of internal standard used	0.1303g	0.1584g	0.1153g	0.1012g
Mass of alkoxide used	0.35g	0.35g	0.2g	0.2g
Mass of cis stilbene produced a	0.1248g	0.1381g	0.1121g	0.1232g
Mass of trans stilbene produced a	0.0818g	0.0922	0.0753g	0.0823g
Yield of stilbenes	0.2066g	0.2303g	0.1874g	0.2055g
Expected yield of stilbenes	0.2055g	0.2303g	0.1916g	0.2018g
% Yield of reaction	100%	100%	98%	102%
Ratio of cis:trans stilbene	1:0.66	1:0.67	1:0.67	1:0.67

a = Average value of 2 injections ± 0.001g

Volume of hexamethylphosphoramide used = $25cm^3$

Mass of benzaldehyde used = 0.9g

Table 24

The results of the Peterson Reaction performed using Phenyl(trimethylsilyl)(tris(p-methylphenyl)silyl)methane

Column used = 10% S.E.30

	Alkoxide used			
	$NaOSiMe_3$	$NaOSiMe_3$	KO^tBu	KO^tBu
Mass of phenyl(trimethylsilyl)(tris(p-methylphenyl)silyl)-methane used	0.5258g	0.5283g	0.5568g	0.5562g
Mass of internal standard used	0.142g	0.1472g	0.1479g	0.1416g
Mass of alkoxide used	0.4g	0.4g	0.25g	0.2g
Mass of cis stilbene produced a	0.1227g	0.1287g	0.1275g	0.1281g
Mass of trans stilbene produced a	0.0800g	0.0813g	0.0819g	0.084g
Yield of stilbenes	0.2027g	0.2100g	0.2094g	0.2121g
Expected yield of stilbenes	0.2042g	0.2051g	0.2162g	0.2160g
% Yield of reaction	99%	102%	97%	98%
Ratio of cis:trans stilbene	1:0.65	1:0.63	1:0.64	1:0.65

a = Average value of 2 injections ± 0.001g

Volume of hexamethylphosphoramide used = $30cm^3$

Mass of benzaldehyde used = 0.9g

Table 25

The results of the Peterson Reaction performed using Phenyl(trimethylsilyl)(triphenylsilyl)methane

Column used = 10% S.E.30

	Alkoxide used					
	NaOMe	NaOMe	$NaOSiMe_3$	$NaOSiMe_3$	KO^tBu	KO^tBu
Mass of phenyl(trimethylsilyl)(triphenylsilyl)-methane used	0.9411g	0.9951g	0.5785g	0.5867g	0.6460g	0.5862g
Mass of internal standard used	0.1417g	0.1494g	0.1533g	0.1504g	0.1464g	0.1190g
Mass of alkoxide used	0.2g	0.2g	0.3g	0.35g	0.2g	0.2g
Mass of cis stilbene produced a	0.2556g	0.2699g	0.1561g	0.1660g	0.1765g	0.1543g
Mass of trans stilbene produced a	0.1286g	0.1415g	0.0917g	0.0959g	0.0979g	0.0858g
Yield of stilbenes	0.3842g	0.4114g	0.2478g	0.2619	0.2744g	0.2401g
Expected yield of stilbene	0.4018g	0.4248g	0.2499g	0.2504	0.2758g	0.2502g
% Yield of reaction	95%	97%	99%	104%	99%	96%
Ratio of cis:trans stilbene	1:0.51	1:0.52	1:0.58	1:0.58	1:0.54	1:0.55

a = Average value of 2 injections $\pm$ 0.001g

Volume of hexamethylphosphoramide used = $30cm^3$

Mass of benzaldehyde used = 0.9g

Table 26

The results of the Peterson Reaction performed using Phenyl(tris(m-fluorophenyl)silyl)(trimethylsilyl)methane

Column used = 10% S.E.30

	Alkoxide used	
	KO^tBu	KO^tBu
Mass of phenyl(tris(m-fluorophenyl)silyl)(trimethylsilyl)methane used	0.5186g	0.5463g
Mass of internal standard used	0.1893g	0.1511g
Mass of cis stilbene produced a	0.1003g	0.1043g
Mass of trans stilbene produced a	0.0860g	0.8095g
Yield of stilbenes	0.1863g	0.1993g
Expected yield of stilbenes	0.1961	0.2066g
% Yield of reaction	95%	96%
Ratio of cis:trans stilbene	1:0.86	1:0.91

a = Average value of 2 injections $\pm$ 0.001g

Volume of hexamethylphosphoramide used = $25cm^3$

Mass of benzaldehyde used = 0.9g

Mass of potassium t-butoxide = 0.18g

Table 27

The results of the Peterson Reaction performed using Phenyl(tris(p-trifluoromethylphenyl)silyl)(trimethylsilyl)methane

Column used = 10% S.E.30

	Alkoxide used	
	KO^tBu	KO^tBu
Mass of phenyl(tris(p-trifluoromethylphenyl)silyl)(trimethylsilyl)methane used	0.5853g	0.6676g
Mass of internal standard used	0.1053g	0.1201g
Mass of cis stilbene produced a	0.0742g	0.0881g
Mass of trans stilbene produced a	0.0873g	0.1077g
Yield of stilbenes	0.1615g	0.1958g
Expected yield of stilbenes	0.1684g	0.1921g
% Yield of reaction	96%	101%
Ratio of cis:trans stilbene	1:1.18	1:1.22

a = Average value of 2 injections ± 0.001g

Volume of hexamethylphosphoramide used = $30cm^3$

Mass of benzaldehyde used = 0.9g

Mass of potassium t-butoxide used = 0.2g

2.13 The effect of oxygen on the α-silylbenzyl carbanion

Dry oxygen was bubbled through a mixture of ice cold bis(trimethylsilyl)phenylmethane (0.8g,3.4mmol) in hexamethylphosphoramide ($25cm^3$). To this sodium silanolate (0.35g,3.1mmol) was added. The reaction mixture initially turned red and after approximately one minute became a pale yellow. The reaction mixture was then worked up as described in Section 2.4. Examination of the reaction mixture by gas liquid chromatography showed that cis and trans stilbenes were produced. The ratio of stilbene products and yield of the reaction is given in Table 28.

Table 28. The Effect of Oxygen on the α-silylbenzyl carbanion.

Mass of bis(trimethylsilyl)phenyl used	0.8043g
Mass of internal standard used	0.1066g
Mass of cis stilbene produced	0.0696g
Mass of trans stilbene produced	0.1024g
Mass of stilbenes expect	0.6138g
% Yield of the reaction	27.7%
Ratio of stilbenes produced	1:1.46

Volume of hexamethylphosphoramide used = $25cm^3$

Mass of sodium silanolate used = 0.35g

Chapter 3 DISCUSSION

3.1 The Objective and Method of Investigating the Peterson Reaction

The objective of this work was to determine the factors that affect the stereochemistry of the olefins produced and the mechanism of the Peterson reaction. Relatively little work had been performed to elucidate the mechanism of the Peterson reaction, most effort being expended in investigating its synthetic utility.

When asymmetrically substituted α-silyl carbanions are reacted with aldehydes it is often found that the product olefins have a cis:trans ratio of 1:1. To investigate which parameters may affect this ratio, it is necessary to employ a reaction system where it is possible to account for all the starting materials. If this is achieved, then it is likely that the observed diastereomeric ratio will reflect the true stereochemical outcome of the system under study.

The first reaction system that was investigated was the formation of stilbenes from an α-silylbenzyl carbanion and benzaldehyde using n-butyllithium and tetramethylethylenediamine to generate the carbanion, as shown in equation (1). This reaction was first performed by Peterson[75] who obtained a yield of 85% and a cis:trans ratio of 1:1.

$$PhCH_2SiMe_3 + PhCHO \xrightarrow[TMEDA]{n\text{-}BuLi} PhCH{=}CHPh \quad (cis:trans = 1:1) \qquad (1)$$

This reaction system was found to be unsuitable for studying the Peterson reaction since the cis:trans ratio and yield of the products were found to be irreproducible. Typical results are given in Table 1.

Table 1. The Results of the Peterson reaction performed using N-Butyllithium and Tetramethylethylene-diamine to generate the α-silyl carbanion.

	% Yield	Ratio of stilbenes cis:trans
1st Reaction	76%	1:0.76
2nd Reaction	46%	1:0.66
3rd Reaction	59%	1:0.54

Products other than stilbenes were also formed. Examination of the reaction mixture by gas chromatographic mass spectrometry indicated that the side products had molecular weights of 268,253,252 and 237. However it was not possible to determine the structures of these products from the mass spectra.

Another reaction system investigated was an adaptation of that of Sakurai.[79] In this method the α-silyl carbanion was generated by reacting bis(trimethylsilyl)phenylmethane with sodium methoxide in hexamethylphosphoramide. The methoxide cleaves one of the trimethylsilyl groups giving an α-silyl carbanion which goes on to react with benzaldehyde to give stilbenes. The reaction is shown below: equation (2).

$$PhCH(SiMe_3)_2 \xrightarrow[HMPA]{NaOMe} Ph\bar{C}HSiMe_3 + PhCHO \longrightarrow PhCH{=}CHPh \quad (2)$$

$$+ \quad MeOSiMe_3 \qquad (\underline{cis}+\underline{trans})$$

It was found that if the benzaldehyde was added to the bis(trimethylsilyl)phenylmethane, in excess, prior to addition of sodium

methoxide, the reaction proceeded to give a 100% yield of stilbenes based on the mass of bis(trimethylsilyl)phenylmethane employed. The yield and ratio of stilbenes produced were examined by means of gas chromatography and using an internal standard. Some idea of the consistency of the results obtained from this reaction system and the accuracy of the method used to examine the yield and the cis:trans ratio of products can be obtained from the results Shown on Table 2.

Table 2. An Examination of the Consistency of the Results obtained from the Peterson reaction.

Experiments Performed	% Yield	Ratio of stilbenes cis:trans
1st Reaction 1st Injection	98.7%	1:1.29
1st Reaction 2nd Injection	98.8%	1:1.29
2nd Reaction 1st Injection	97.7%	1:1.33
2nd Reaction 2nd Injection	98.6%	1:1.32

It has also been possible to show that in this system, the stilbenes produced do not undergo isomerization. This was achieved by adding known quantities of cis stilbene or trans stilbene to the reaction mixture, of bis(trimethylsilyl)phenylmethane and benzaldehyde in hexamethylphosphoramide, prior to addition of sodium methoxide. The work up was performed in the usual manner and the quantities of cis and trans stilbene present were determined by gas chromatography. By subtracting the amount of stilbene added to the reaction mixture it was possible to determine the ratio of products produced by the Peterson reaction. The results obtained are given in Table 3.

Table 3. An Investigation of possible Isomerization of Stilbene Products.

Mass of bis(trimethylsilyl)phenylmethane used.	Mass of stilbene added	Calculated % Yield	Calculated Ratio of stilbenes cis:trans
0.4498g	0.0477g (trans)	100%	1:1.35
0.5343g	0.0781g (trans)	100%	1:1.32
0.5999g	0.1081g (cis)	101%	1:1.32
0.6604g	0.2310g (cis)	103%	1:1.33

The calculated ratio of stilbenes are very similar to those given in Table 2, showing that under the conditions of the reaction the stilbenes produced do not isomerize.

It has also been shown that varying the alkoxide used to generate the α-silyl carbanion has no effect on the diastereoisomeric ratio of stilbenes produced. Results obtained using sodium methoxide, sodium propoxide and sodium silanolate are given in Table 4.

Table 4. The effect of different alkoxides on the diastereoisomeric ratio of stilbenes produced by the Peterson Reaction.

Alkoxide used to generate the α-silyl carbanion	% Yield	Ratio of Stilbenes cis:trans
NaOMe	99%	1:1.32
$NaO^{n}Pr$	99%	1:1.33
$NaOSiMe_3$	100%	1:1.30

These results indicate that irrespective of the alkoxide a free carbanion is being formed. This is consistent with the work of Eaborn[116] who showed that the methanolysis of benzyltrimethylsilane with methanol gave a free carbanion.

To conclude, since this system gives almost quantitative yields of the products and reproducible cis:trans ratio, it is possible to determine the various factors which may affect the stereochemical outcome of the Peterson reaction. Thus, the Peterson reaction has been performed using different counterions, at various temperatures, in different solvents in the presence of salts and with different groups attached to the silicon. The results of these experiments are given in the following sections.

3.2 The Effect of Temperature on the Peterson Reaction

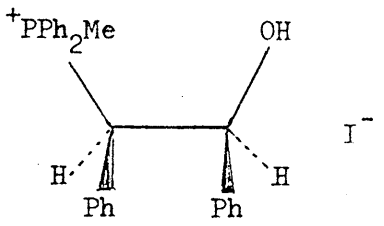
These experiments were performed by allowing the reaction mixture to reach the required temperature and then adding the sodium methoxide. To reduce the possibility of isomerization of the stilbenes, the reaction mixture was only allowed to stand for one minute before being worked up. The results obtained are given in Table 5.

Table 5. The Effect of Temperature on the diastereoisomeric ratio of stilbenes produced by the Peterson Reaction.

Temperature of the reaction	% Yield	Ratio of stilbenes (cis:trans)
5°C	97%	1:1.25
26°C	99%	1:1.32
46°C	98%	1:1.33
76°C	99%	1:1.39

Unfortunately, it was not possible to perform the Peterson reaction at a temperature lower than 5°C, because the hexamethylphosphoramide solidifies below this temperature.

From these results it is apparent that the ratio of stilbenes is largely unaffected by changing the temperature of the reaction, since only a small increase in the proportion of trans olefin is produced. This is unlike the Wittig reaction in which a large change in the cis:trans ratio of stilbenes is observed as the temperature of the reaction is raised. Trippett[37] treated the salt LXIX with base in different solvents at different temperatures and measured the ratio of cis:trans stilbenes produced.



LXIX

These results were compared with those obtained when benzylidenediphenylmethylphosphorane was reacted with benzaldehyde under the same conditions. Using these two sets of results given in Table 6, it is possible to determine the ratio k_2/k_3 which represents the degree of reversibility of the erythro isomer as shown in Scheme 1.

Scheme 1.

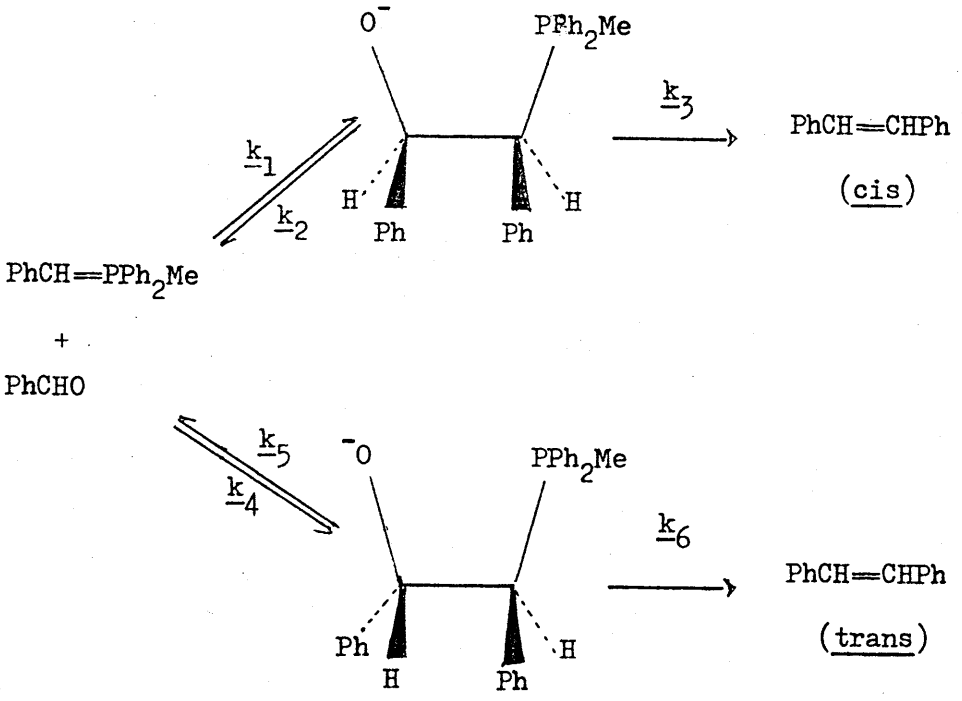


Table 6. The Effect of Temperature on the Stereochemistry of the Wittig Reaction.

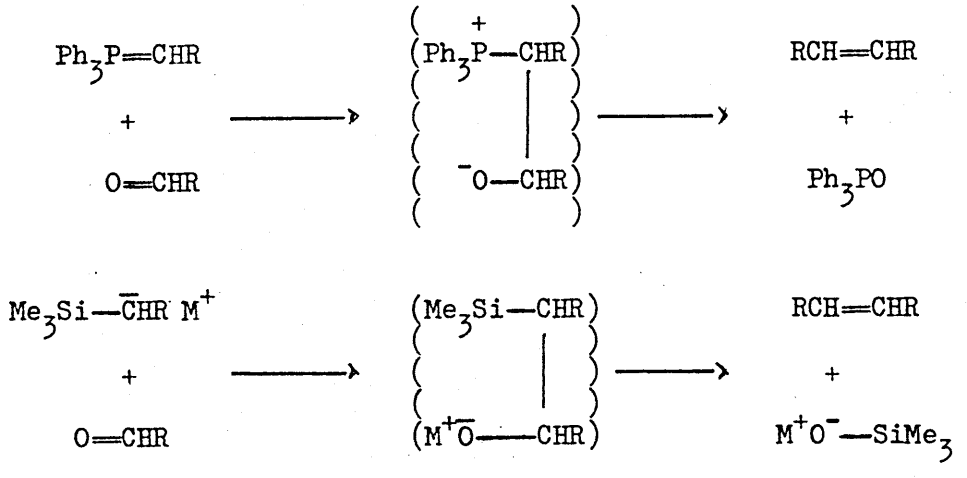
Reaction system studied	Solvent used	Temperature of reaction	Ratio of stilbenes cis:trans	Calculated value for k_2/k_3
Salt (LXIX)	EtOH	0°C	1:0.23	0.37
$PhCH{=}PPh_2Me$ + PhCHO	EtOH	0°C	1:2.49	
Salt (LXIX)	EtOH	24.4°C	1:0.56	0.99
$PhCH{=}PPh_2Me$ + PhCHO	EtOH	24.4°C	1:2.57	
Salt (LXIX)	EtOH	50.5°C	1:0.92	1.9
$PhCH{=}PPh_2Me$ + PhCHO	EtOH	50.5°C	1:2.70	
Salt (LXIX)	MeOH	0°C	1:1.17	3.0
$PhCH{=}PPh_2Me$ + PhCHO	MeOH	0°C	1:2.57	
Salt (LXIX)	MeOH	24.4°C	1:1.40	3.25
$PhCH{=}PPh_2Me$ + PhCHO	MeOH	24.4°C	1:3.54	
Salt (LXIX)	MeOH	50.5°C	1:1.63	3.4
$PhCH{=}PPh_2Me$ + PhCHO	MeOH	50.5°C	1:4.0	
Salt (LXIX)	THF	0°C	1:0.05	0.13
$PhCH{=}PPh_2Me$ + PhCHO	THF	0°C	1:0.66	
Salt (LXIX)	THF	24.4°C	1:0.08	0.17
$PhCH{=}PPh_2Me$ + PhCHO	THF	24°C	1:0.88	
Salt (LXIX)	THF	50.5°C	1:0.09	0.22
$PhCH{=}PPh_2Me$ + PhCHO	THF	50.5°C	1:0.92	

As the temperature of the reaction mixture is increased the proportion of trans stilbene produced increases. This can be explained in terms of an increased dissociation of the intermediate betaine to starting materials as indicated by the increasing value of k_2/k_3. However in the Peterson reaction, the cis:trans ratio of stilbenes produced is relatively independent of temperature suggesting the irreversible nature of the Peterson reaction.

3.3 The Effect of Different Counterions and the addition of Salts on the Stereochemical outcome of the Peterson Reaction.

There are many differences between the Wittig and Peterson reactions. One such difference is that in the Peterson reaction a metal cation carries the counter positive charge associated with the α-silyl carbanion but in the Wittig reaction no such counterion is present and the reaction can be carried out in salt free media. This difference is illustrated in Scheme 2.

Scheme 2.

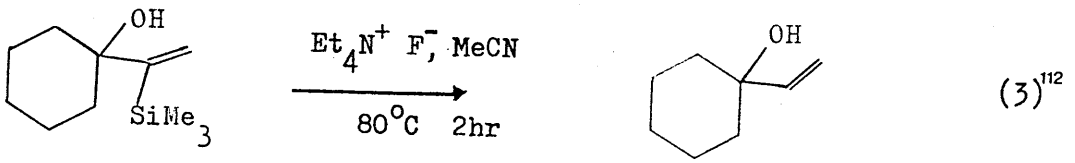


The effect of different counterions on the stereochemistry of the Peterson reaction has not been extensively investigated by other research workers. We have carried out such a study using different alkoxides to generate the α-silyl carbanion. The results are shown in Table 7.

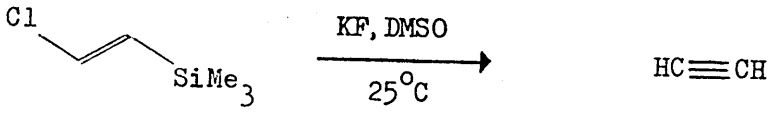
Table 7. The Effect of Different Counterions on the Diastereoisomeric Ratio of Stilbenes produced by the Peterson Reaction.

Alkoxide used to generate the α-silyl carbanion	% Yield	Ratio of stilbenes cis:trans
LiO^tBu	100%	1:1.43
NaOMe	99%	1:1.32
KO^tBu	100%	1:1.30

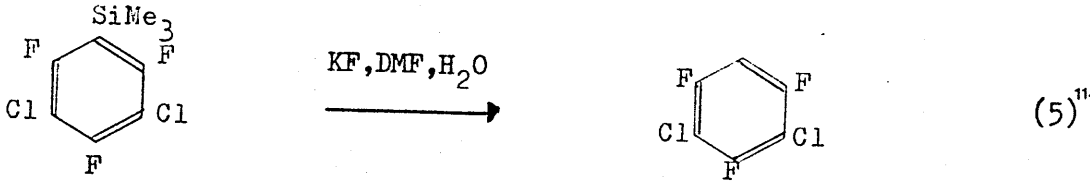
Attempts to generate the α-silyl carbanion using lithium methoxide or magnesium methoxide failed. This is most probably due to the poor solubility of these oxides. Fluoride ions have also been used to eliminate trimethylsilyl groups from silicon containing compounds. Typical examples are shown in equations 3-5.



(3)[112]



(4)[113]



(5)[114]

However, in this system, treatment of bis(trimethylsilyl)phenylmethane with potassium and ceasium fluoride did not generate the α-silyl carbanion.

From the results given in Table 7, it is apparent that the use of potassium as the counterion gives very similar results to sodium. However, when lithium is used as the counterion, there is a small but

measurable increase in the proportion of trans olefin. This small effect may be due to increased association of the lithium cation with α-silyl carbanion or the oxygen of the benzaldehyde.

The effect of the magnesium cation on the stereochemistry of the Peterson reaction was examined in two ways. One method involves carrying out the Peterson reaction in the presence of magnesium iodide. This was done by dissolving one equivalent of magnesium iodide with bis(trimethylsilyl)phenylmethane and benzaldehyde in hexamethylphosphoramide prior to addition of sodium silanolate. The other method involved preparing a solution of the α-silyl carbanion by adding sodium silanolate to bis(trimethylsilyl)phenylmethane in hexamethylphosphoramide. To this solution was added one equivalent of magnesium iodide followed by benzaldehyde. The result of this latter experiment can be compared with the result of a similar experiment in which the α-silyl carbanion solution was prepared in the absence of the magnesium ion and then quenched with benzaldehyde. Comparison of these two sets of results enables the effect of magnesium to be measured.

Table 8. The Effect of Magnesium Iodide on the Peterson Reaction.

Method employed to examine the Peterson reaction	% Yield	Ratio of Stilbenes cis:trans
α-silyl carbanion solution quenched with benzaldehyde.	54%	1:1.24
Peterson reaction performed in the presence of MgI_2	56% 33%	1:1.81 1:1.63
MgI_2 added to α-silyl carbanion solution prior to quenching with PhCHO	54%[1] 19%[2]	1:1.96 1:1.76

1 Quenched after 2 minutes. 2 Quenched after 15 minutes.

The experiment carried out in the absence of magnesium iodide gave a cis:trans ratio of stilbenes which was very similar to those shown in Table 4, obtained when sodium silanolate was used to generate the α-silyl carbanion in the presence of benzaldehyde. This shows that the cis:trans ratio of stilbenes is relatively independent of how the reaction is performed. However, when the α-silyl carbanion is generated in the absence of benzaldehyde, the yield of the reaction is only 54%. This reduced yield is probably due to abstraction of hydrogen atoms from the solvent by the α-silyl carbanion.

The addition of magnesium iodide to the Peterson reaction appears to result in an increase in the proportion of trans stilbene. This occurs when the magnesium iodide is present as a salt in the reaction mixture or when it is added to a solution of preformed α-silyl carbanion. It is however, difficult to draw any definite conclusion from these results since the yields of the reactions are so low. This differs from previous work on the Peterson reaction where the use of magnesium as the counterion results in an increased proportion of cis olefin. This was attributed to the magnesium preferentially stabilizing the transition state of the irreversible first step leading to the cis olefin.[98] It is not possible to compare these results with similar studies of the Wittig reaction since such data is not available.

The Peterson reaction has also been studied in the presence of added lithium and sodium salts. The salt under consideration was dissolved in hexamethylphosphoramide along with the bis(trimethylsilyl)phenylmethane and benzaldehyde prior to addition of alkoxide. The results of these studies are shown in Table 9.

Table 9. The Effect of addition of Lithium and Sodium Salts on the Diastereoisomeric Ratio of Stilbenes obtained from the Peterson Reaction.

Salt used	Mass of salt added[a]	Alkoxide used	% Yield	Ratio of stilbenes cis:trans
Lithium iodide	0g (0.0)	NaOMe	98%	1:1.32
"	0.1g (0.34)	"	103%	1:1.31
"	0.3g (0.91)	"	72%	1:1.45
"	0.9g (3.8)	"	26%	1:11.4
Lithium perchlorate	0g (0.0)	LiO^tBu	100%	1:1.43
"	0.2g (0.95)	"	90%	1:1.42
"	0.4g (1.98)	"	71%	1:1.45
"	0.8g (3.96)	"	53%	1:1.47
Sodium tetraphenylboron	0g (0.0)	NaOMe	98%	1:1.32
"	0.2g (0.31)	"	94%	1:1.20
"	0.6g (0.9)	"	90%	1:1.16
"	1.2g (1.76)	"	98%	1:1.13

a = The equivalents of salt added with respect to bis(trimethylsilyl)phenylmethane are given in parenthesis.

The results given in Table 9 show that the addition of salts to the Peterson reaction has very little effect on the cis:trans ratio of stilbenes produced. Only when a large excess of lithium iodide was added to the reaction mixture was a substantial increase in the proportion of trans stilbene observed. However, the yield of this reaction was low, thus it was not possible to draw any conclusions from this result.

Whereas in the Peterson reaction the stereochemistry appears to be independent of the addition of salts, this is not the case for the Wittig reaction. The Wittig reaction can be performed in salt free media or in the presence of various salts. In the case of reactions of non-stabilized ylids with aldehydes in non-polar solvents, the addition of lithium salts causes an increase in the proportion of trans olefin being produced.[115] This is illustrated by Table 10.

Table 10. The Effect of Addition of Salts on the Diastereoisomeric Ratio of Alkenes obtained by the Wittig Reaction.

$Ph_3P{=}CHCH_3 + PhCHO \longrightarrow Ph_3PO + CH_3CH{=}CHPh$

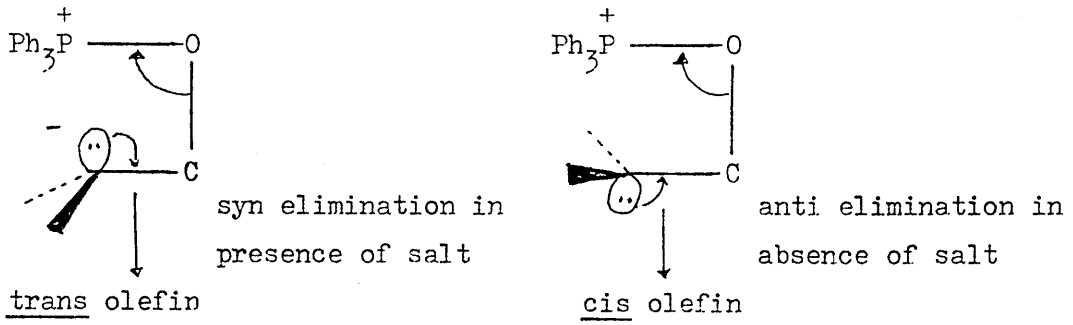
Solvent = Benzene/light petroleum

Salt present	% Yield	cis:trans ratio of olefin
-	98%	1:0.15
LiCl	70%	1:0.23
LiBr	68%	1:0.64
LiI	76%	1:0.74
$LiBPh_4$	63%	1:1

Two proposals have been put forward to explain these results. Firstly, it was proposed that the lithium salt could complex with the intermediate betaine and stabilize it.[39] This stabilization would promote the reversibility of the reaction and hence allow more of the

thermodynamically favoured trans olefin to be produced. The alternative proposal, made by Whangbo,[66] is that the elimination of triphenylphosphine oxide could be affected by the lithium salts in the same way that Elcb eliminations[71] are. This is illustrated in Scheme 2.

Scheme 2.



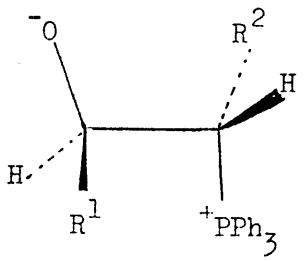
In the case of reactions of semi-stabilized ylids with aldehydes in non-polar solvents the addition of lithium salts increases the proportion of cis olefin being produced.[41] Typical results are given in Table 11.

Table 11. The Effect of Addition of Salts on the Diastereoisomeric Ratio of Alkenes obtained from the Wittig Reaction.

$Ph_3P{=}CHPh + EtCHO \longrightarrow Ph_3P{=}O + PhCH{=}CHEt$

Salt present	Solvent	cis:trans ratio of olefins
-	Benzene	1:4.55
LiCl	Benzene	1:3.76
LiBr	Benzene	1:2.70
LiI	Benzene	1:1.44
-	Hexane	1:3.55
LiCl	Hexane	1:3.35
LiI	Hexane	1:2.23
-	Ether	1:3.35
LiCl	Ether	1:3.76
LiI	Ether	1:2.03

To explain these results Bergelson proposed that Lewis acids such as Lithium iodide could complex with the intermediate betaine, reducing the electrostatic attraction between the phosphorus and oxygen atoms. This promotes formation of the anti-periplanar conformation LXX, which results in an increased proportion of the cis olefin being formed.



LXX

However, in the case of reactions of semi-stabilized ylids with aldehydes in polar aprotic solvents, the presence or absence of salts has very little effect on cis:trans ratio of the olefins produced.[41] This is shown by the results given in Table 12.

Table 12. The Effect of Addition of Salts on the Diastereoisomeric Ratio of Alkenes obtained from the Wittig Reaction.

$Ph_3P{=}CHPh + EtCHO \longrightarrow Ph_3P{=}O + PhCH{=}CHEt$

Salt present	Solvent	cis:trans ratio of olefins
-	DMF	1:1.44
LiCl	DMF	1:1.56
LiBr	DMF	1:1.56
NaBr	DMF	1:1.63
KBr	DMF	1:1.56
LiI	DMF	1:1.27

From our studies of the Peterson reaction it is apparent that the stereochemistry is relatively unaffected by the addition of salts to the reaction media. This may be because, unlike the Wittig reaction, a metal cation must always be present in the Peterson reaction and thus the presence of excess salt has little effect.

3.4 The Diastereoisomeric Ratio obtained from the Peterson Reaction performed in Tetrahydrofuran/Hexamethylphosphoramide solvent systems.

The effect of solvent on the stereochemistry of the Peterson reaction has not been studied previously by other research workers. Using a mixture of hexamethylphosphoramide and tetrahydrofuran, it has been possible to investigate how the stereochemistry of the Peterson reaction is affected by changes in the polarity of the solvent. The results obtained are given in Table 13.

Table 13. The Results of the Peterson Reaction performed in Tetrahydrofuran/Hexamethylphosphoramide solvent systems.

Alkoxide used	% Tetrahydrofuran in solvent mix.	% Yield	Ratio of Stilbenes cis:trans
Li O^{t}Bu	0%	100%	1:1.43
"	20%	98%	1:1.33
"	40%	58%	1:1.27
NaOMe	0%	98%	1:1.32
"	20%	103%	1:1.30
"	40%	99%	1:1.36
"	50%	98%	1:1.48
"	70%	70%	1:1.52
K O^{t}Bu	0%	100%	1:1.28
"	20%	98%	1:1.31
"	40%	98%	1:1.32
"	60%	97%	1:1.29
"	80%	96%	1:1.33

From these results it is apparent that performing the Peterson reaction in tetrahydrofuran/hexamethylphosphoramide solvent systems of varying composition, has very little effect on the cis:trans ratio of stilbenes produced. When lithium is the counterion there is a small but measurable increase in the proportion of the cis olefin, whereas with sodium as the counterion, an increase in the proportion of trans olefin is observed. With potassium as the counterion, the stilbene cis:trans ratio appears to be unaffected even when the solvent comprises 80% tetrahydrofuran. The other noticeable trend apparent in these results is the effect on the yield of the reaction of increasing the proportion of tetrahydrofuran in the solvent. With potassium as the counterion the yield of the reaction is greater than 95% even when the solvent is 80% tetrahydrofuran, whereas with lithium the yield of the reaction is greatly diminished when the solvent comprises only 40% tetrahydrofuran. The yields obtained in each reaction probably reflect the solubility of the alkoxide in the solvent.

The effect of other solvents on the Peterson reaction has also been investigated. These results are given in Table 14.

Table 14. The Effect of Solvent on the Diastereoisomeric Ratio of Stilbenes obtained by the Peterson Reaction.

Solvent used	Alkoxide used	% Yield	Ratio of Stilbenes cis:trans
Dimethylformamide	$NaOSiMe_3$	96%	1:1.14
"	NaO^nPr	88%	1:1.13
Dimethylsulphoxide	$NaOSiMe_3$	99%	1:1.20
"	KO^tBu	97%	1:1.32
Tetrahydrofuran	KOMe [a]	88%	1:1.44
"	KOMe [a]	87%	1:1.43

a = Performed in the presence of 1 equivalent of 18-Crown-6 Ether

From these results it is again apparent that using different solvents has very little effect on the diastereoisomeric ratio of stilbenes produced. Attempts at performing the Peterson reaction in acetonitrile or hexane (with a crown ether) failed.

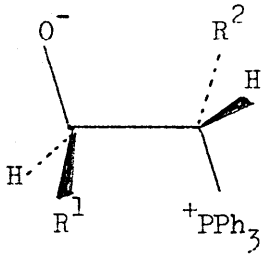
Again, the effect of varying the solvent on the diastereoisomeric ratio of stilbenes produced, differs in the Wittig and Peterson reactions. The Wittig reaction using non-stabilized ylids can only be performed in aprotic solvents and is largely unaffected by changes in solvent. With semi-stabilized ylids the Wittig reaction can also be performed using protic solvents and it is generally found that polar solvents increase the proportion of cis olefin being produced.[41] Typical results are given in Table 15.

Table 15. The Effect of Solvent on the Diastereoisomeric Ratio of Alkenes obtained from the Wittig Reaction.

Phosphorus ylid used.	Aldehydes used.	Solvent used	Ratio of Olefins cis:trans
$Ph_3P{=}CHEt$	EtCHO	DMF	1:0.075
$Ph_3P{=}CHEt$	EtCHO	Benzene	1:0.087
$Ph_3P{=}CHPh$	EtCHO	Benzene	1:4.43
$Ph_3P{=}CHPh$	EtCHO	Hexane	1:3.52
$Ph_3P{=}CHPh$	EtCHO	Ether	1:3.5
$Ph_3P{=}CHPh$	EtCHO	DMF	1:1.56
$Ph_3P{=}CHPh$	PhCHO	Benzene	1:1.94
$Ph_3P{=}CHPh$	PhCHO	EtOH	1:0.85[54]

It has been proposed[41] that the increase in cis olefin formation occurs in polar or protic solvents because increased solvation of the intermediate betaine reduces electrostatic attraction between the

phosphorus and oxygen. This results in a greater proportion of the anti-periplanar conformation LXX and hence the cis olefin is favoured.



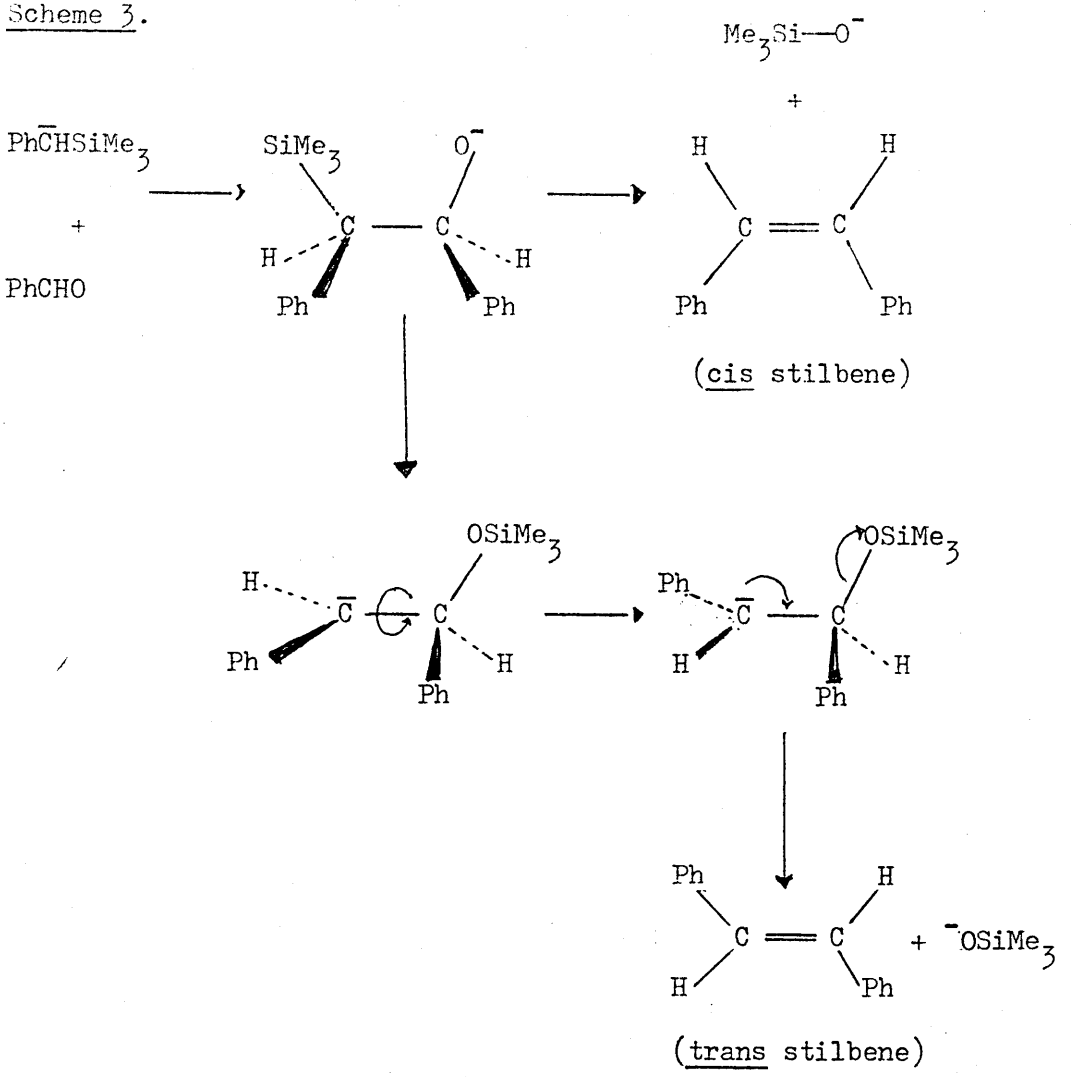
LXX

The results obtained for the Peterson reaction demonstrate that the addition of salts or changing the solvent have very little effect on the diastereoisomeric ratio of olefins produced. This indicates that the Peterson reaction is not reversible and that the stereochemistry of the reaction is determined by the rapid initial combination of the reactants. The results also indicate that the relative energies of the transition states leading to the intermediates are unaffected by changes in the polarity of the reaction media.

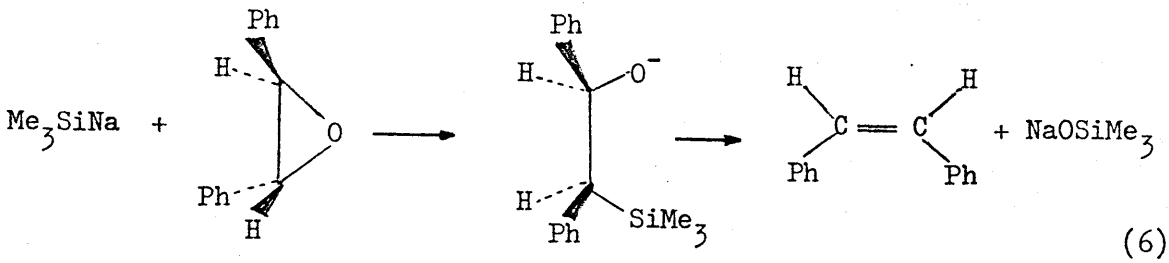
3.5 An Investigation of the Mechanism of the Elimination of the Silanolate anion.

The elimination of the silanolate anion has been shown to occur in a syn fashion and to be a synchronous event when the α-silyl carbanion is not stabilized by an electron withdrawing group.[92] This was shown by the work of Peter Shippey[93] who reacted trimethylsilyl potassium with trans-3-hexene oxide and obtained only cis-3-hexene. In this present work however, the α-silyl carbanion is partially stabilized by a phenyl group. If the trimethylsilyl group migrates to oxygen prior to elimination of silanolate, it is possible that rotation about the carbon-carbon bond might occur enabling a mixture of products to be formed. This proposal is analogous to the mechanism suggested by Bestmann[62] for the Wittig reaction and is shown in Scheme 3.

Scheme 3.

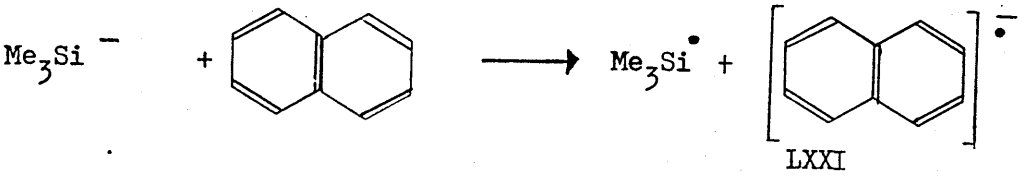


To examine whether cleavage of the silicon-carbon bond occurs in advance of the carbon-oxygen bond in the Peterson reaction under study, trimethylsilyl sodium was reacted with trans stilbene oxide in hexamethylphosphoramide. The reaction was performed by adding sodium methoxide to hexamethydisilane to generate the trimethylsilyl sodium, followed by addition of an excess of trans stilbene oxide. If elimination of the silanolate is a synchronous event only cis stilbene should be formed as shown in equation 6.

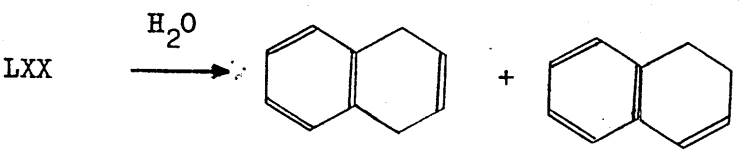


(6)

However, the major products of this reaction, which was repeated many times, were bibenzyl and 1-trimethylsilyl-1,2 diphenylethane. It is thought that these are formed because, in hexamethylphosphoramide, trimethylsilyl sodium acts as a good electron donor, rather than a nucleophile.[117,118] An example of a reaction involving the trimethylsilyl anion as an electron donor is shown in equation 7.



LXXI



13% 11%

An analogous system has been studied by Rfftz[119] who reacted dimethylphenylsilyllithium with cis or trans stilbene oxide in tetrahydrofuran. The results are given in Table 12.

Table 12. The Results of Reactions between Dimethylphenylsilyllithium and Stilbene Oxide

Epoxide used	Olefin produced	% Yield	% Product geometry
trans stilbene oxide	cis stilbene	75%	97%
cis stilbene oxide	trans stilbene	83%	99%

From these results it is apparent that in this system the intermediate produced, when dimethylphenylsilyllithium reacts with trans stilbene oxide, undergoes stereospecific syn elimination of silanolate to give cis stilbene. Even if the silicon carbon bond cleavage is advanced with respect to the carbon oxygen bond cleavage it would appear that the elimination of silanolate occurs faster than the rotation of the carbon carbon bond. Thus, the stereochemistry of the reaction between a benzyltrimethylsilyl anion and benzaldehyde is determined by the initial approach of the reactants to one another.

3.6 Oxidation of α-silylbenzyl carbanions

Phosphorus ylids can be decomposed by oxygen[120] or peracetic acid[121] to give a phosphine oxide and an aldehyde or ketone. The carbonyl compounds produced can then undergo the Wittig reaction with ylids, that have not been decomposed by oxygen, to give alkenes.

$$Ph_3P{=}CHR + O_2 \longrightarrow Ph_3PO + RCHO \xrightarrow{Ph_3P{=}CHR} 2Ph_3PO + RCH{=}CHR \qquad (8)$$

R = alkyl or phenyl (50%)

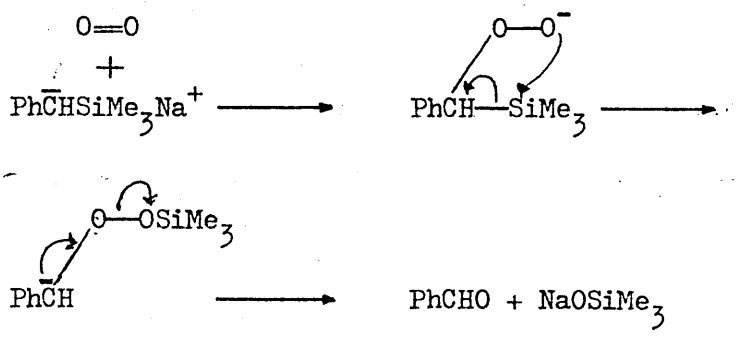
In view of these results, a similar experiment was carried out in which oxygen was bubbled through a solution of the α-silylbenzyl carbanion in hexamethylphosphoramide. The result obtained is given in Table 13.

Table 13. Oxidation of α-silylbenzyl carbanions.

Silane used	Alkoxide used	Stilbene % Yield	Ratio of stilbenes cis:trans
$PhCH(SiMe_3)_2$	NaOMe	28%	1:1.45

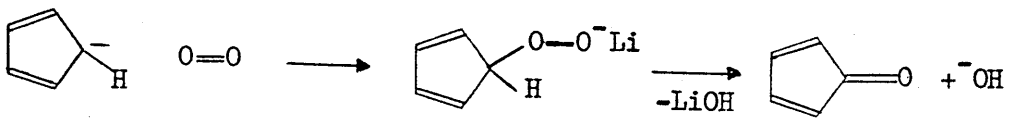
The yield of this reaction was only 28% and does not approach the 50% obtained when the corresponding phosphorus ylid was oxidised. A possible reason for this may be that α-silyl carbanions are more easily quenched by extraction of a proton from the solvent than are phosphorus ylids. However, the ratio of cis and trans stilbenes produced is very similar to that obtained when an α-silylbenzyl carbanion was reacted with benzaldehyde (Section 3.1 Table 4). This result indicates that the oxidation of an α-silylbenzyl carbanion gives benzaldehyde which upon further reaction with an α-silylbenzyl carbanion gives stilbenes. A possible mechanism for this oxidation is given in Scheme 4.

Scheme 4.



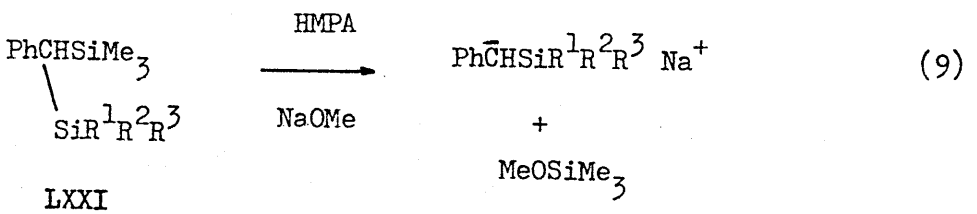
This mechanism for the oxidation of an α-silyl carbanion is analogous to that proposed by Davis[122] for the oxidation of a cyclopentadienyl carbanion as illustrated in Scheme 5.

Scheme 5.



3.7 The effect of different alkyl and aryl groups attached to the silicon atom on the Stereochemistry of the Peterson Reaction.

The effect of changing the groups attached to the silicon atom was examined by placing sterically bulky groups about one of the silicon atoms in the starting material LXXI. This prevents nucleophilic attack by alkoxide anions and results in the preferential removal of the less sterically hindered silicon atom which bears three methyl groups. This is illustrated in equation 9.



(9)

The use of sterically bulky groups attached to the silicon atom to reduce nucleophilic attack of hydroxide or alkoxide anions is well known. Tert-butyldimethylsilyl groups are frequently used as hydroxyl protecting groups that are stable under alkali conditions. Eaborn[123] has also carried out experiments that illustrate the effect of

changing the groups attached to the silicon on the rate of hydrolysis of alkynyl silanes as shown in Table 14.

Table 14. Comparison of Rates of Nucleophilic Substitution of some Alkynyl Silanes[123]

$$R^1R^2R^3SiC{\equiv}CPh \xrightarrow{^-OH,MeOH} R^1R^2R^3SiOH + {}^-C{\equiv}CPh$$

Substituent Groups $R^1R^2R^3$	k rel
Me_3	277
Me_2Et	49
$MeEt_2$	74
Et_3	1
$^iPr_3$	0.00074

In each of the experiments performed in this work, unless otherwise stated, the trimethylsilyl group was eliminated preferentially. This was confirmed by treating a solution of the silicon compound under consideration, with alkoxide to give an α-silyl carbanion. The reaction mixture was then quenched with dilute hydrochloric acid, extracted with dichloromethane and examined by g.l.c., showing the presence of R_3SiCH_2Ph and no Me_3SiCH_2Ph.

The results of Peterson reactions in which the groups about the silicon atom were varied are given in Table 15. The trends observed in these results can be rationalized by considering the factors which influence the formation of the intermediate.

Table 15. The Effect of Varying the Groups about the Silicon Atom on the Stereochemistry of the Peterson Reaction.

The α-silyl carbanion that was used took the form $PhC\bar{H}SiR^1R^2R^3\ M^+$

Nature of Groups attached to the silicon atom.	Alkoxide used to generate the α-silyl carbanion	% Yield	Ratio of stilbenes (cis:trans)
$R^1=R^2=R^3=Me$	LiO^tBu	100%	1:1.43
$R^1=R^2=R^3=Me$	NaOMe	98%	1:1.32
$R^1=R^2=R^3=Me$	NaO^nPr	99%	1:1.33
$R^1=R^2=R^3=Me$	$NaOSiMe_3$	100%	1:1.30
$R^1=R^2=R^3=Me$	KO^tBu	100%	1:1.28
$R^1=R^2=R^3=Et$	$NaOSiMe_3$	99%	1:1.24
$R^1=R^2=R^3=Et$	KO^tBu	100%	1:1.26
$R^1=Me, R^2=R^3=\ ^iBu$	$NaOSiMe_3$	94%	1:1.15
$R^1=Me, R^2=R^3=$ cyclohexyl	$NaOSiMe_3$	93%	1:1.14
$R^1=R^2=Me, R^3=\ ^tBu$	LiO^tBu	101%	1:1.10
$R^1=R^2=Me, R^3=\ ^tBu$	NaOMe	98%	1:1.04
$R^1=R^2=Me, R^3=\ ^tBu$	KO^tBu	99%	1:1.12
$R^1=R^2=Ph, R^3=\ ^tBu$	LiO^tBu	35%	1:0.71
$R^1=R^2=Ph, R^3=\ ^tBu$	$NaOSiMe_3$	96%	1:0.65
$R^1=R^2=Ph, R^3=\ ^tBu$	NaOMe	96%	1:0.66
$R^1=R^2=Ph, R^3=\ ^tBu$	KO^tBu	96%	1:0.75

Contd..

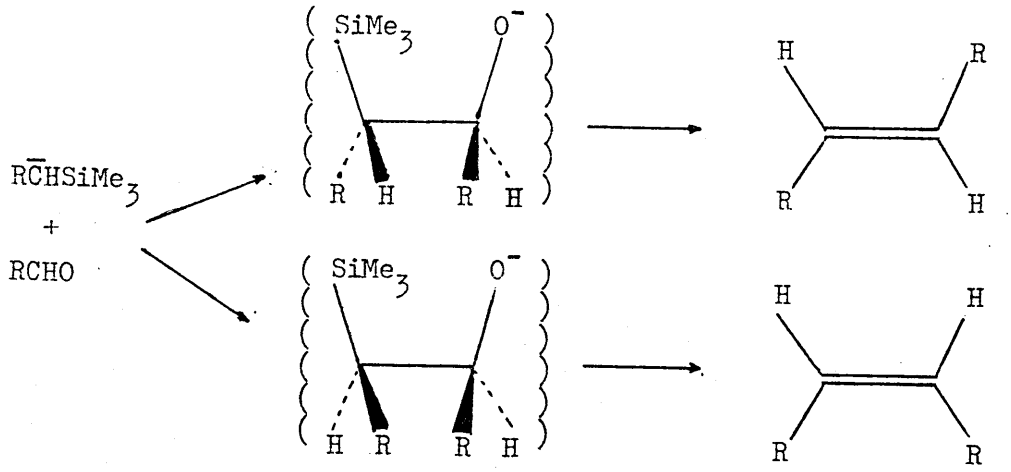
Table 15 contd.

Nature of Groups attached to the silicon atom.	Alkoxide used to generate the α-silyl carbanion	% Yield	Ratio of stilbenes (cis:trans)
$R^1=R^2=R^3=C_6H_4OMe\text{-}p$	$NaOSiMe_3$	100%	1:0.66
$R^1=R^2=R^3=C_6H_4OMe\text{-}p$	KO^tBu	100%	1:0.67
$R^1=R^2=R^3=C_6H_4CH_3\text{-}p$	$NaOSiMe_3$	101%	1:0.64
$R^1=R^2=R^3=C_6H_4CH_3\text{-}p$	KO^tBu	97%	1:0.64
$R^1=R^2=R^3=C_6H_5$	NaOMe	96%	1:0.52
$R^1=R^2=R^3=C_6H_5$	$NaOSiMe_3$	102%	1:0.58
$R^1=R^2=R^3=C_6H_5$	KO^tBu	98%	1:0.54
$R^1=R^2=R^3=C_6H_4F\text{-}p$	KO^tBu	95%	1:0.89
$R^1=R^2=R^3=C_6H_4CF_3\text{-}p$	KO^tBu	98%	1:1.18

3.8 Factors that may Influence the Stereochemistry of the Peterson Reaction

In the Peterson reaction α-silyl carbanions react with carbonyl compounds to give a diastereoisomeric mixture of β-silyl alkoxides which undergo stereospecific syn elimination of silanolate to give the product olefins.[92] This is illustrated in Scheme 6.

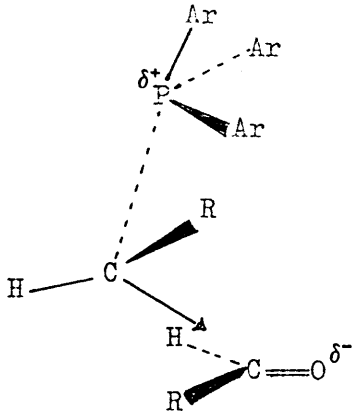
Scheme 6.



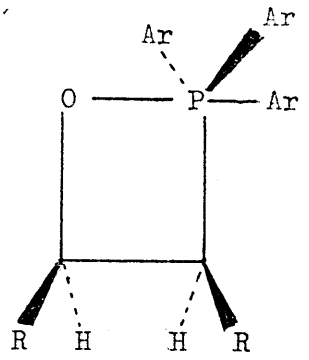
The stereospecific nature of the elimination of the silanolate has been proved by the work of Rfftz[119] where R represents phenyl rings. Thus the ratio of cis and trans olefins produced by the Peterson reaction is dependent on the relative rates of formation of the β-silyl alkoxides intermediates. This in turn is dependent on the relative energies of the transition states leading to the β-silyl alkoxides. Therefore the ratio of cis and trans olefins produced reflects the relative energies of the transition states.

This is in contrast with the mechanism put forward by Bestmann[62] to explain the stereochemistry of the Wittig reaction. In this proposal the phosphorus ylid and carbonyl compound are believed to react together via a betaine-like transition state LXXII, to give only the cis

oxaphosphetane intermediate LXXIII. It is the mode of decomposition of this intermediate that is thought to determine the stereochemistry of the product olefin.



LXXII



LXXIII

From the results given in Table 15 it is apparent that increasing the steric bulk of the groups about the silicon atom increases the proportion of cis stilbene that is produced. This trend is illustrated in Table 16. A similar effect has been observed by Allen[53] for the Wittig reaction as described in Section 1.3.

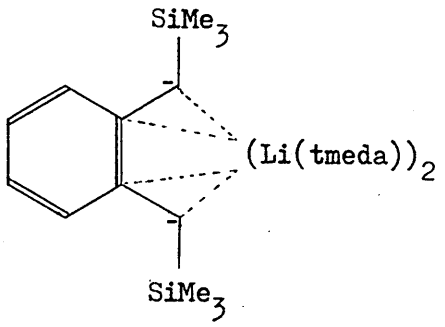
Table 16. The effect of increasing the Steric Bulk of the Silicon Atom on the cis:trans ratio of stilbenes produced.

Nature of α-silylbenzyl carbanion prepared $PhC\bar{H}SiR^1R^2R^3$ Na^+

The nature of the groups attached to the silicon atom	% Yield	Ratio of Stilbenes cis:trans
$R^1=R^2=R^3=Me$	100%	1:1.30
$R^1=R^2=R^3=Et$	99%	1:1.24
$R^1=R^2={}^iBu, R^3=Me$	94%	1:1.15
$R^1=R^2=$cyclohexyl, $R^3=Me$	93%	1:1.14
$R^1=R^2=Me, R^3={}^tBu$	98%	1:1.04
$R^1=R^2=Ph, R^3={}^tBu$	96%	1:0.65
$R^1=R^2=R^3=Ph$	96%	1:0.55

To account for these results it is necessary to consider the factors which may be important in determining the manner in which the two reactants approach one another and their effect on the relative energies of the two transition states. To determine the preferred conformation of any possible transition state leading to a β-silyl alkoxide it is necessary to first consider the ground state structure of the reactants. The benzaldehyde is of course planar, however, unlike the phosphorus ylids of the Wittig reaction, very little is known about the nature of the α-silyl carbanions. However, the crystalline structure of LXXIV has been determined which showed the α-silyl carbanion to be planar.[81] This is believed to be due to the carbanion being stabilized by the phenyl ring.

LXXIV



In the case of the α-silylbenzyl carbanion used in these experiments MNDO calculations have also shown the carbanion to be planar. The results of these calculations are given in Table 17 and illustrated in figure 1.

Table 17. Results of MNDO Calculations on the α-silylbenzyl Carbanion

Atom Number I	Type of Atom	Bond Length (Angstroms) J I	Bond Angle (Degrees) K J I	Twist Angle (Degrees) L K J I	J	K	L
1	C						
2	Si	1.788			1		
3	C	1.871	113.12		2	1	
4	H	1.106	109.83	-.47	3	2	1
5	H	1.106	112.96	119.21	3	2	1
6	H	1.106	112.47	239.98	3	2	1
7	C	1.872	106.79	119.79	2	3	4
8	H	1.107	112.41	5.55	7	2	3
9	H	1.106	112.43	126.14	7	2	3
10	H	1.105	111.51	245.27	7	2	3
11	C	1.871	108.21	234.37	2	3	4
12	H	1.107	112.53	3.07	11	2	3
13	H	1.104	110.62	123.25	11	2	3
14	H	1.107	112.28	242.69	11	2	3
15	H	1.093	111.28	120.63	1	2	3
16	C	1.387	131.68	59.74	1	2	3
17	C	1.452	121.66	180.16	16	1	2
18	C	1.388	122.59	179.97	17	16	1
19	C	1.406	120.27	-.04	18	17	16
20	C	1.407	120.01	-.04	19	18	17
21	C	1.394	119.58	-.08	20	19	18
22	H	1.092	118.59	-.06	17	16	1
23	H	1.093	120.16	180.04	18	17	16
24	H	1.090	119.87	179.95	19	18	17
25	H	1.092	120.09	180.03	20	19	18
26	H	1.091	117.84	179.86	21	20	19

L K J I represents the number of the atom under consideration.

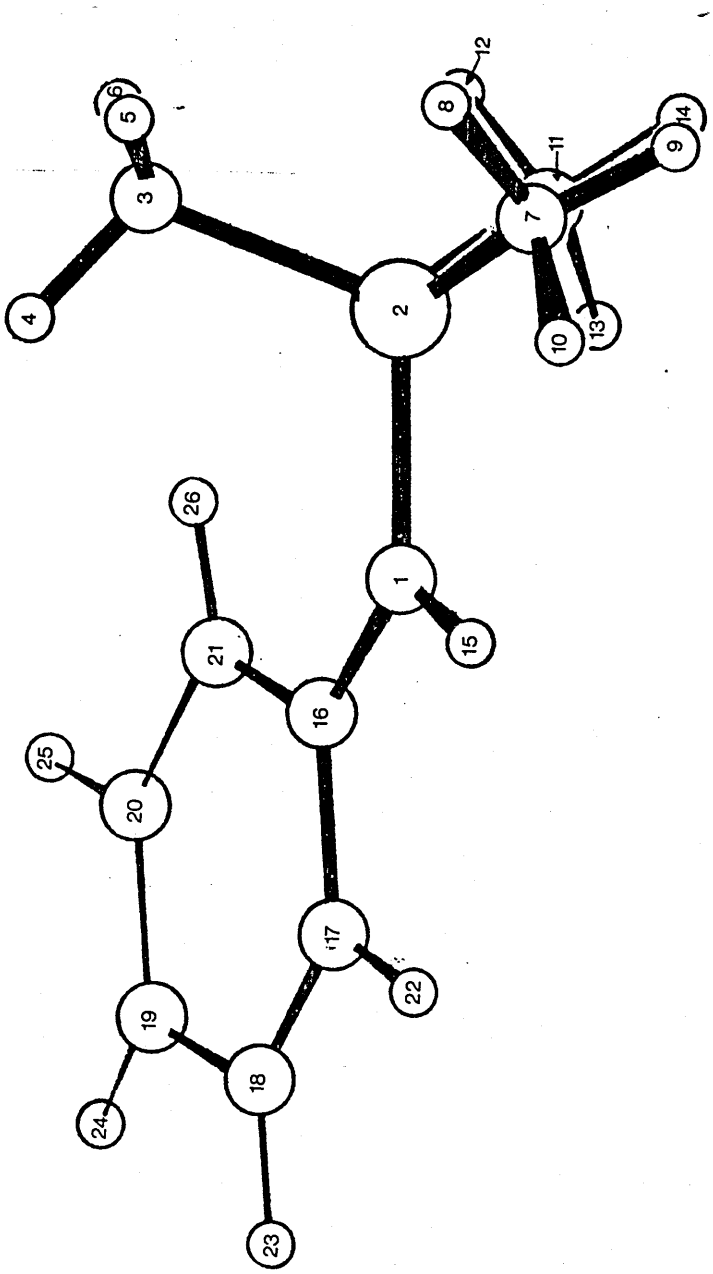
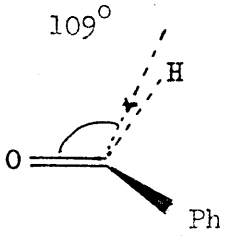


Figure 1. The conformation of an α-silylbenzyl carbanion determined by MNDO calculations.

Next, the orientation of the approach of the two reactants must be examined. It has been shown by Dunitz that a nucleophile approaches a carbonyl compound at an angle of 109°.[124,125] Thus it is expected that the α-silyl carbanion will attack the benzaldehyde in a similar fashion.

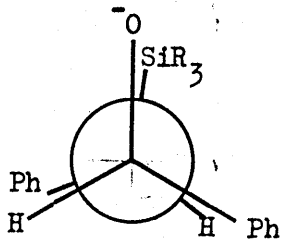


Approach of nucleophile

Finally, it is necessary to consider the conformation of the various groups about the axis of attack. To a first approximation this can be obtained by studying the interactions that are present in the intermediate. However, the dangers of such an approximation must be borne in mind as there will always be specific interaction in the transition state which will not be present in the intermediate and vice versa. The possible conformation of the β-silyl alkoxide are shown in Scheme 7.

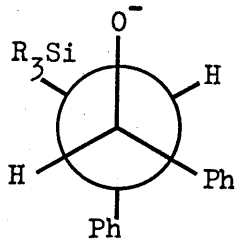
Scheme 7.

LXXV



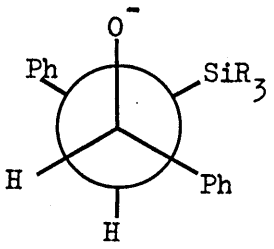
trans stilbene

LXXVI



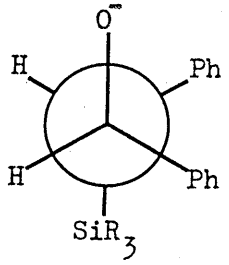
trans stilbene

LXXVII



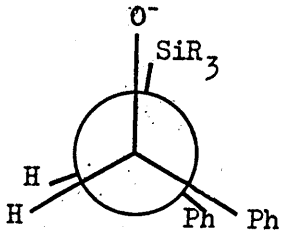
trans stilbene

LXXVIII



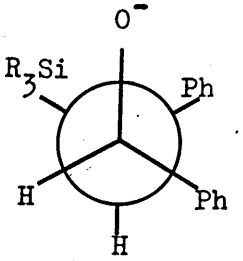
trans stilbene

LXXIX



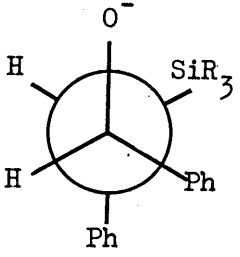
cis stilbene

LXXX



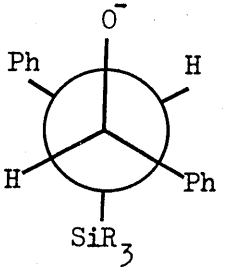
cis stilbene

LXXXI



cis stilbene

LXXXII

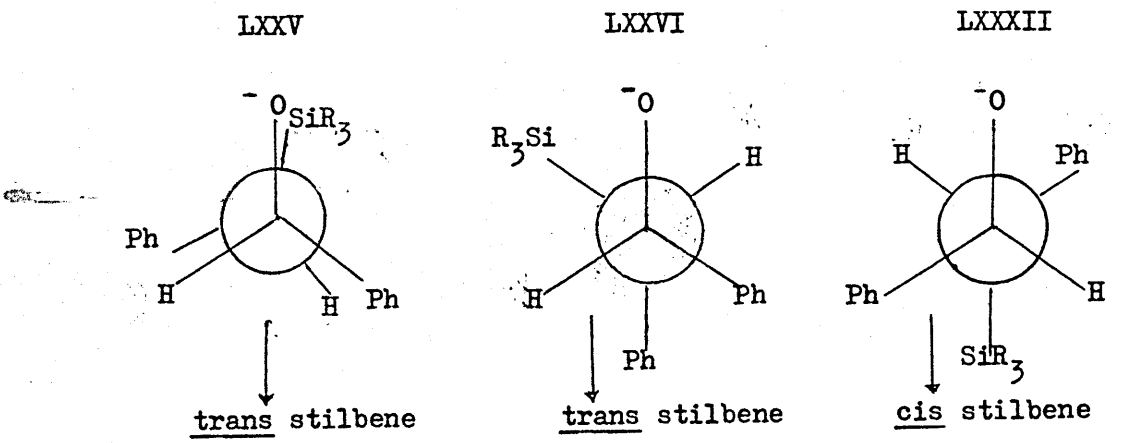


cis stilbene

From an examination of these conformations it would appear that the threo intermediate might be produced via a transition state with a conformation which lies somewhere between LXXV and LXXVI. The exact nature of this transition state would depend on the degree of the silicon-oxygen interaction and steric repulsion between the phenyl rings and the hydrogen atoms. The conformations LXXVII and LXXVIII should be of higher energy owing to the gauche interactions of the oxygen, phenyl and silyl groups which are not present to the same extent in the conformation LXXVI. When considering the transition state leading to the formation of the erythro intermediate it appears that the conformation LXXXII would be the most favoured form which gives cis stilbene. The formation of the erythro intermediate via a transition state with a conformation of LXXIX is very unlikely owing to the eclipsing of phenyl rings. The conformations LXXX and LXXXI would also be expected to be unfavourable, in the same way as has been argued for LXXVII and LXXVIII.

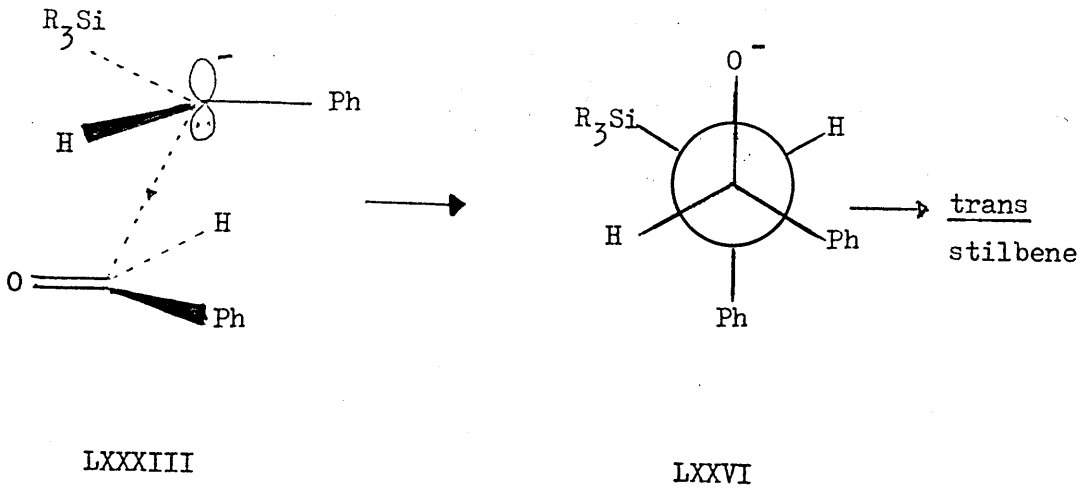
Using this line of reasoning it would appear that the transition state leading to trans stilbene has a conformation somewhere between LXXVI and LXXV and that the cis stilbene is formed via a transition state of conformation LXXXII. This is illustrated by Scheme 8.

Scheme 8.

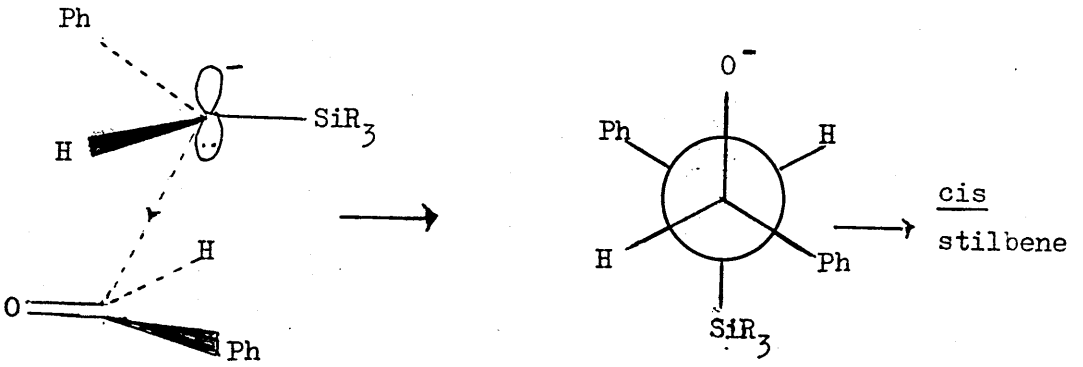


The results of Table 16 show that increasing the steric bulk of the groups attached to the silicon increases the proportion of cis stilbene that is produced. This means that the energy of the transition state LXXXII leading to the erythro intermediate is lowered relative to the energy of the transition state LXXV/LXXVI leading to the threo isomer. This is reasonable if the transition state leading to the threo intermediate resembles LXXV, since increasing steric bulk around the silicon atom should disfavour LXXV more than LXXXII. However, if the transition state leading to the threo form is more like LXXVI, the results are difficult to explain. The steric interaction between the silyl group and the phenyl ring of the benzaldehyde in LXXXII would be expected to be greater than that between the silyl group and the oxygen atom in LXXVI and the threo intermediate rather than the erythro intermediate would be favoured. One possible discrepancy is that the planar reactants combine in a parallel fashion with the carbon of the carbanion displaced behind that of the benzaldehyde as illustrated in Scheme 9.

Scheme 9.



LXXXIII LXXVI



LXXXIV LXXXII

When the reactants approach each other in the manner shown by LXXXIII some steric interaction between the silyl group and the hydrogen atom of the benzaldehyde would be expected to occur. As the steric bulk of the silyl group is increased this interaction would also be expected to increase. This in turn would lead to an increasing proportion of the reactants combing in the manner shown by LXXXIV with the silyl group projecting well away from the benzaldehyde. Hence an increased proportion of cis stilbene would be expected.

The formation of cis and trans stilbenes can thus be represented by the energy diagrams given in figures 2 and 3.

Figure 2. Energy Diagram for the Formation of Trans Stilbene

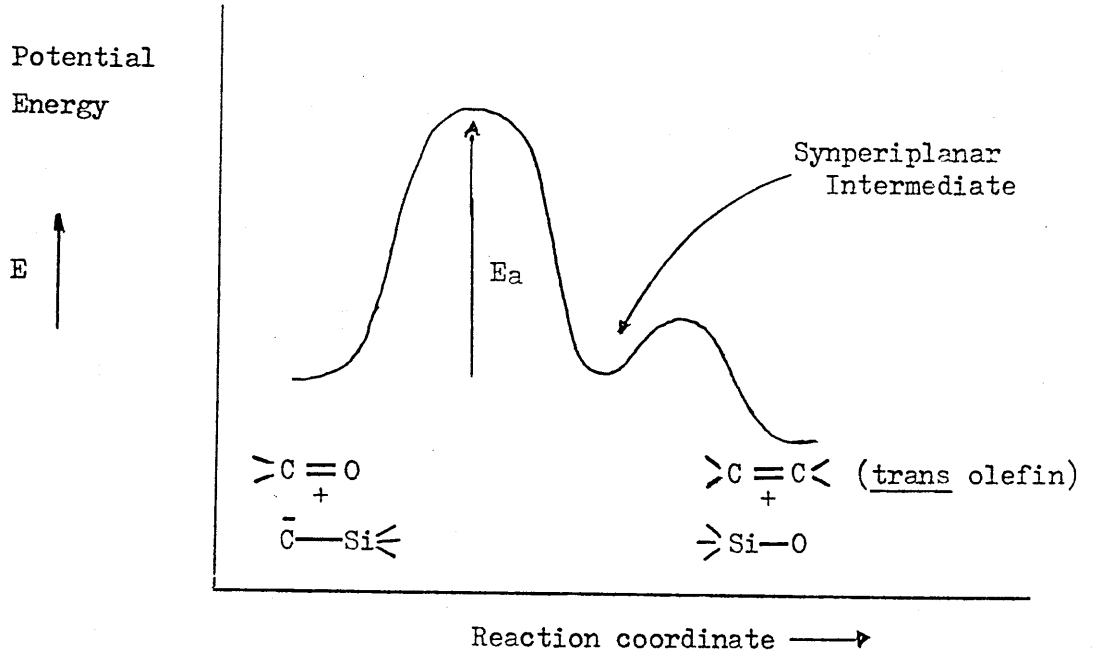
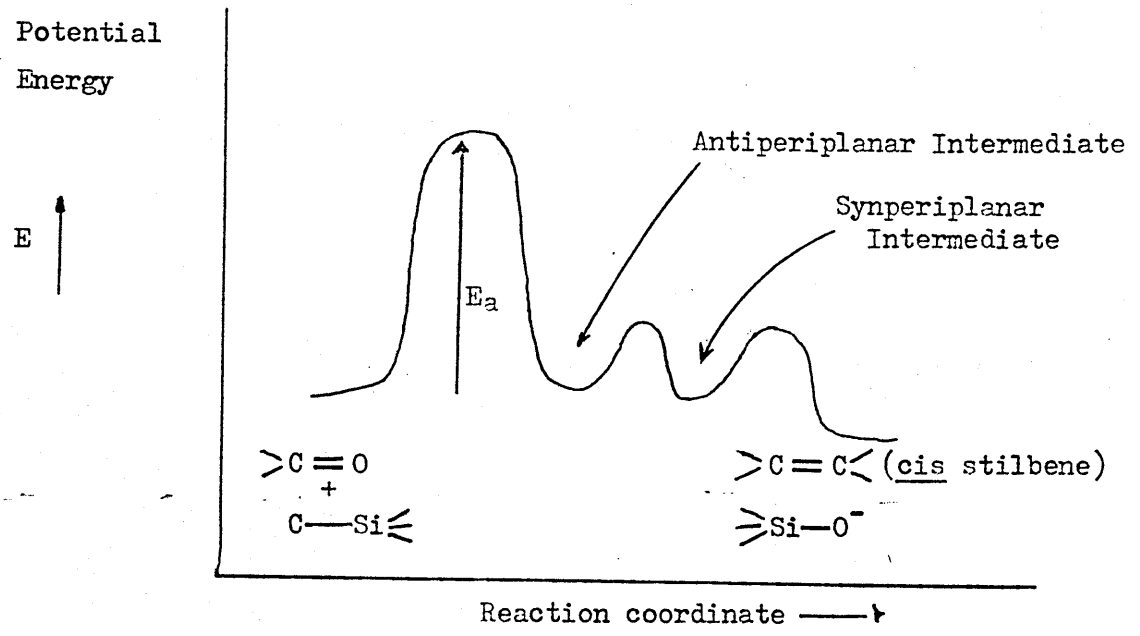
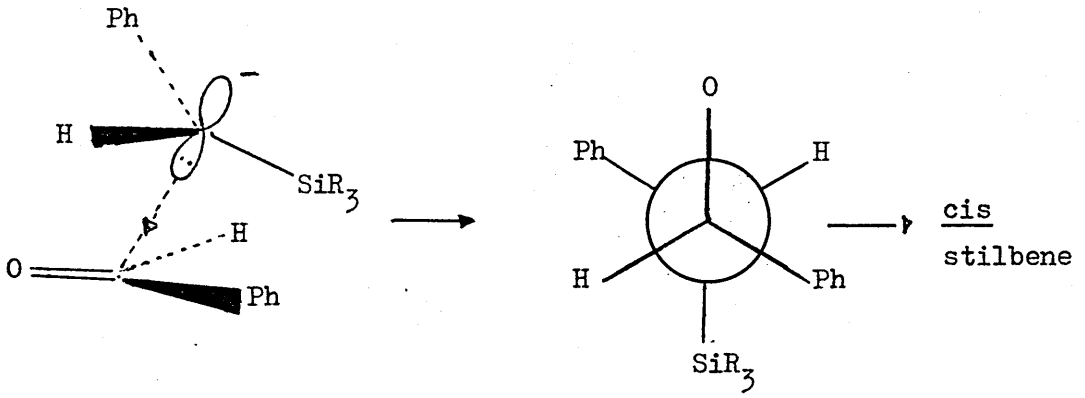


Figure 3. Energy Diagram for the Formation of Cis Stilbene



However, in many ways, this approach is fairly unsatisfactory. One reason for this is that, as stated, there may be interactions present in the transition state which are not reflected in the intermediate. Dunitz has shown that the lone pair of the nucleophile is directed towards the carbon atom of the carbonyl group at an angle of 109°.[125] Therefore, it is more accurate to illustrate the reactants combining to give the β-silyl alkoxide LXXXII via a transition state looking like LXXXV with the p-orbital coincident with the axis of attack as shown in Scheme 10.

Scheme 10.

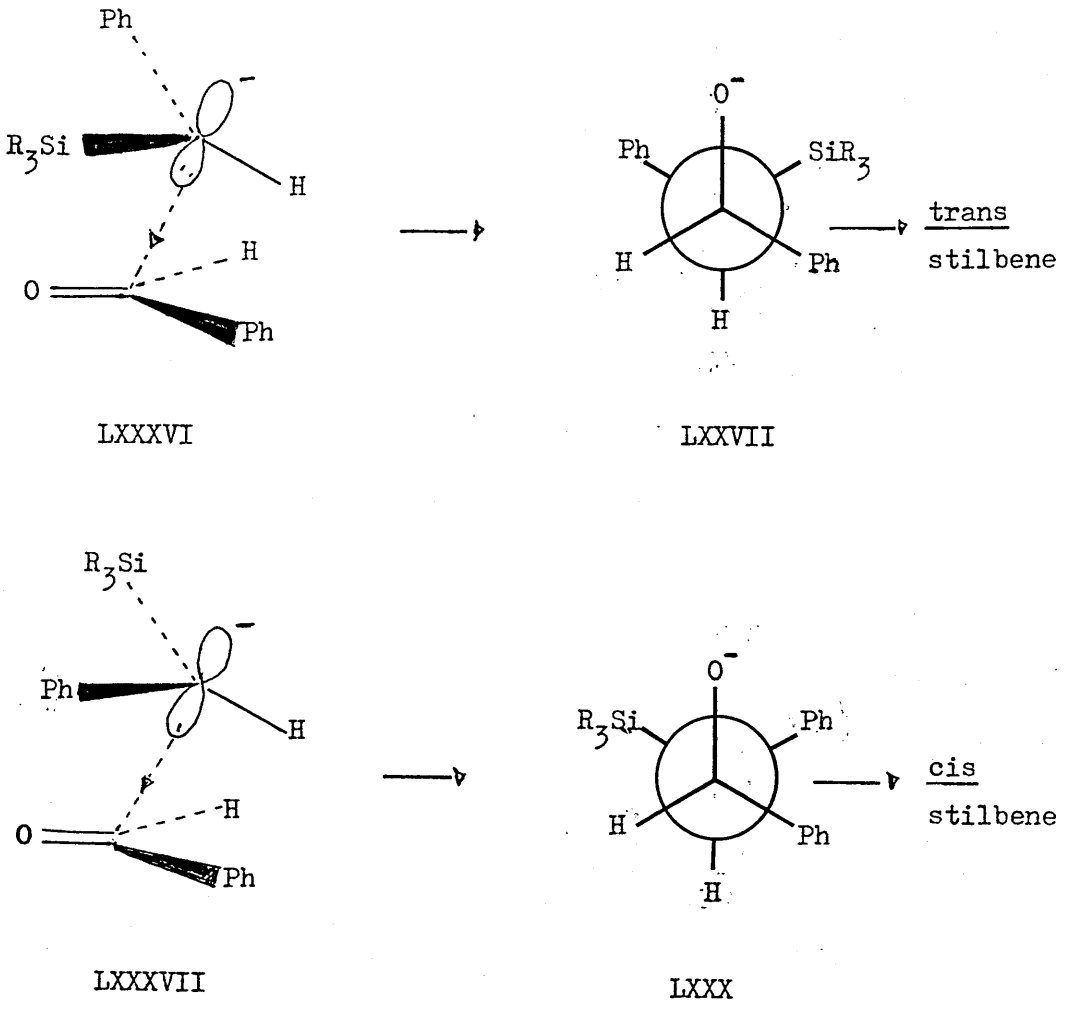


LXXXV LXXXII

In the transition state shown by LXXXV it is apparent that the silyl group is projected down towards the phenyl ring and hydrogen atom of the benzaldehyde. This should result in steric interactions which would be very different from those present in the intermediate β-silyl alkoxide. A similar effect would also be observed if the phenyl group were pointing towards the benzaldehyde. A more likely

form of the transition states is illustrated in Scheme 11.

Scheme 11.



LXXXVI LXXVII

LXXXVII LXXX

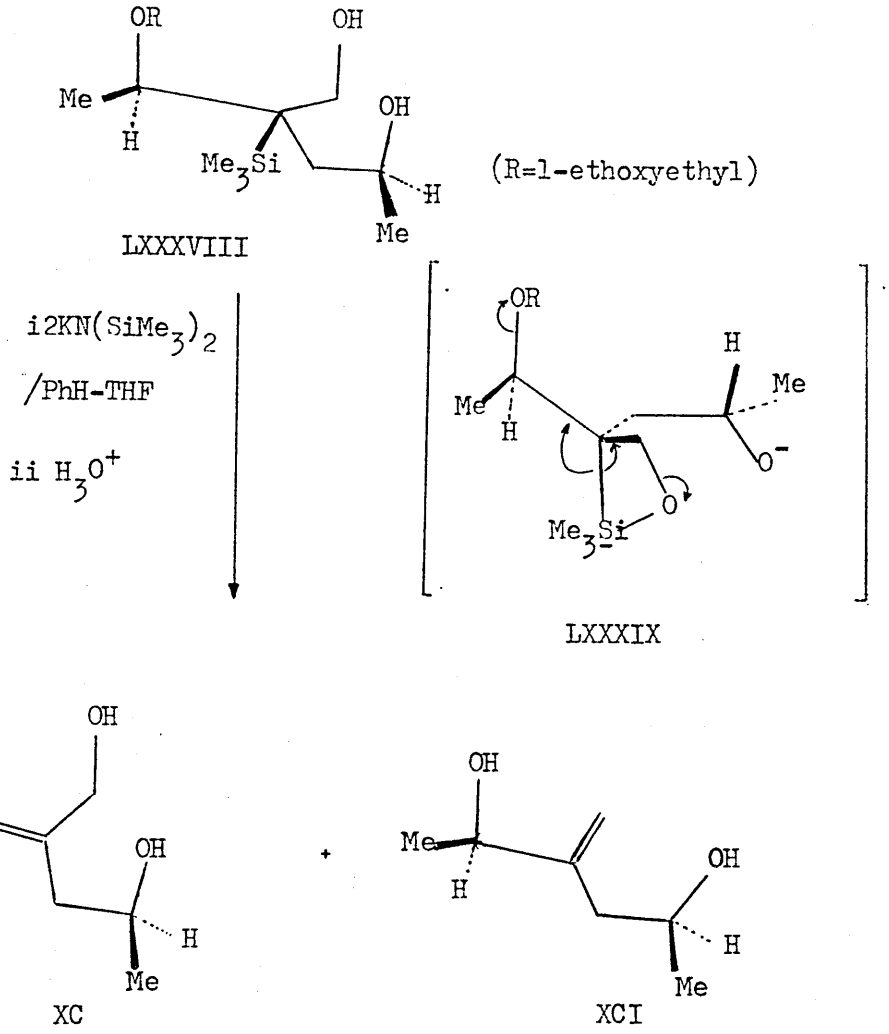
In each of the transition states LXXXVI and LXXXVII it is the hydrogen atom of the α-silylbenzyl carbanion which projects towards the phenyl ring and hydrogen atom of the benzaldehyde. In this manner the steric interaction that occurs in LXXXV is avoided. From Scheme 11 it is apparent that the relative proportions of cis and trans stilbene will be dependent on the size of the steric interaction between the silyl group and phenyl ring in LXXXVI relative to steric interaction between the phenyl rings in LXXXVII. Now it is expected that as the steric bulk of the silyl group increases, so the gauche

interaction with the phenyl ring would increase and it would become favourable for reactants to combine in the manner shown by LXXXVII. This in turn would result in an increased proportion of cis stilbene being formed as observed experimentally.

Earlier it was mentioned that the degree of silicon-oxygen interaction will effect the conformation of the transition state leading to the β-silyl alkoxide. In salt free Wittig reactions it is thought that there is a strong electrostatic attraction between the positively charged phosphorus atom and the negatively charged oxygen atom which results in the transition state having a synperi-planar conformation. In silicon chemistry although it is known that a silicon-oxygen bond is strong ($530 kJmol^{-1}$), there is not a great deal of evidence that suggests that silicon-oxygen interaction may occur in the transition state of the Peterson reaction.

Recently, it has been proposed that in order to explain the reaction shown in Scheme 12, the β-silyl alkoxide may exist as a penta-coordinate species.[126]

Scheme 12.

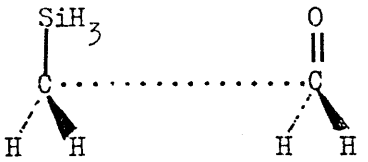


The formation of both XC and XCI can best be explained in terms of the formation of the penta-coordinate silicon species LXXXIX.

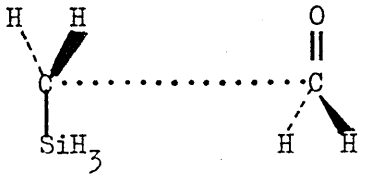
To determine whether such an interaction could exist, some MNDO calculations have been performed. These calculations involve bringing a model α-silyl carbanion, $^{-}CH_2SiH_3$, together with formaldehyde to give an intermediate with a synperiplanar or anti-

periplanar conformation as illustrated in Scheme 13.

Scheme 13.



Synperiplanar Conformation



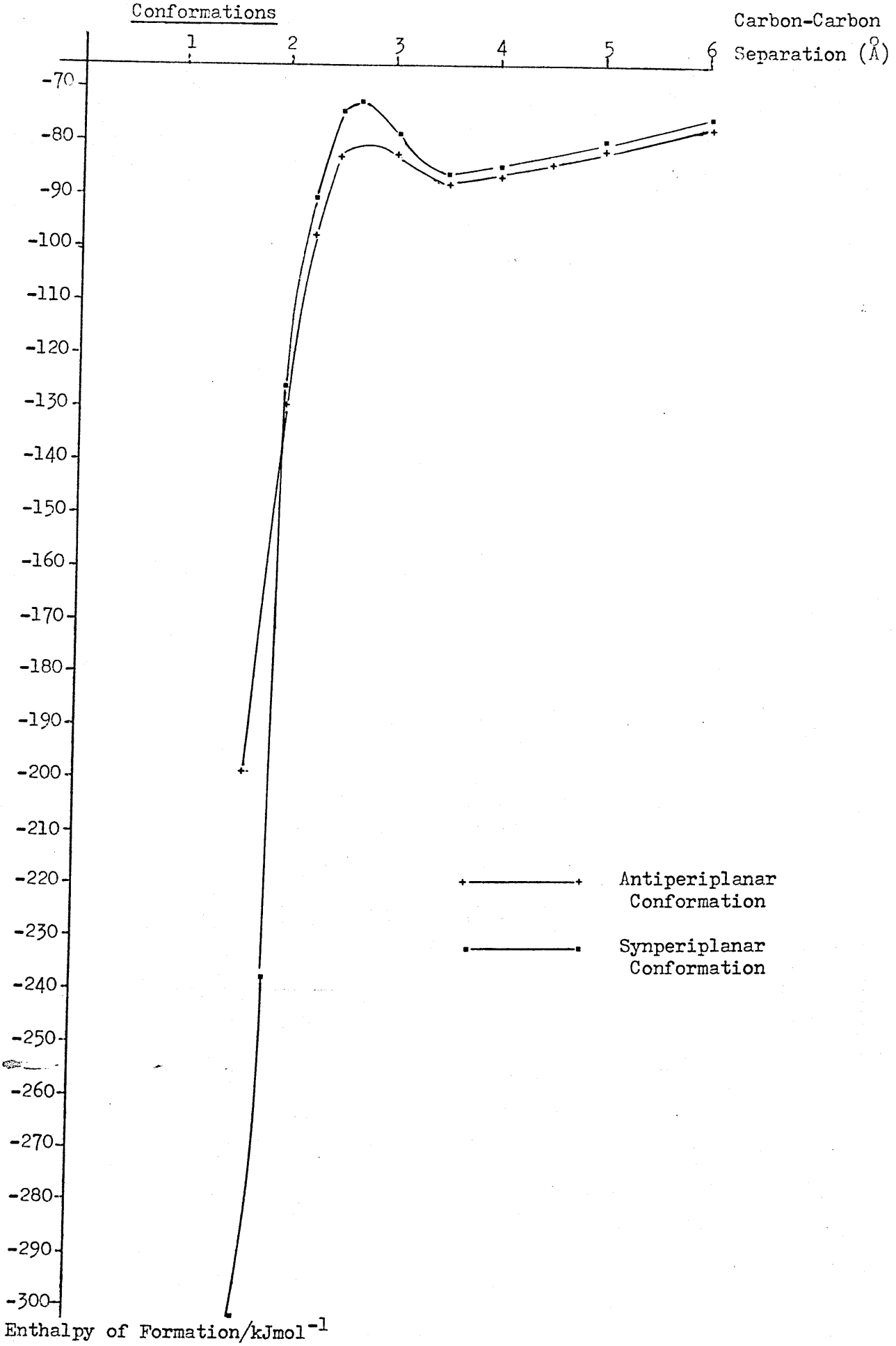
Antiperiplanar Conformation

By carrying out these calculations with the carbon atoms of the reactants at varying distances it has been possible to show that the enthalpy of formation of the synperiplanar conformation of the intermediate would be expected to be more negative than that of its antiperiplanar conformation. These results are given in Table 18 and illustrated by Graph 1.

Table 18. The effect of varying the carbon-carbon separation on the Heat of Formation of the Synperiplanar or Antiperiplanar Conformations

Carbon-Carbon Separation (Å)	Heat of Formation of the Synperiplanar Conformation. ($kJmol^{-1}$)	Heat of Formation of the Antiperiplanar Conformation ($kJmol^{-1}$)
1.55	-302.02	–
1.60	–	-198.66
1.8	-237.09	-172.66
2.0	-124.32	-129.70
2.2	-91.77	-98.7
2.5	-73.58	-81.94
2.65	-72.79	–
3.0	-77.7	-81.61
3.5	-85.89	-86.27
4.0	-84.50	-85.80
4.5	–	-83.41
5.0	-79.93	-81.34
6.0	-75.6	-78.71
8.0	-71.4	-72.828

Graph 1. The effect of varying the carbon carbon separation on the Enthalpy of Formation of the Synperiplanar or Antiperiplanar Conformations



The MNDO calculations also give the bond lengths and bond angles of the synperiplanar and antiperiplanar intermediates. These results are given in Tables 19 and 20 and are illustrated in Figure 2.

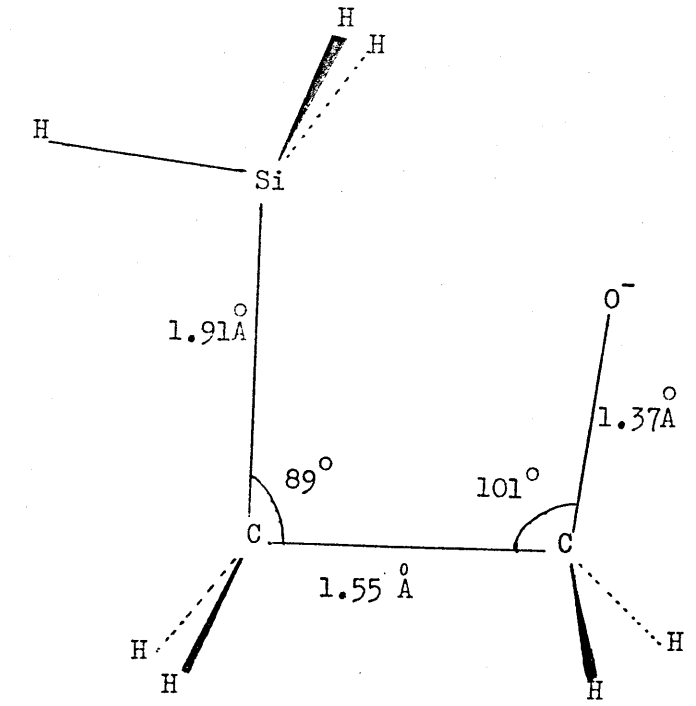
Table 19. Bond Lengths and Bond Angles of the Synperiplanar Conformation

Atom Number I	Type of Atom	Bond Length (Angstroms) JI	Bond Angle (Degrees) KJI	Twist Angle (Degrees) LKJI	J K L
1	Si				
2	C	1.910			1
3	C	1.552	88.51		2 1
4	O	1.372	101.93	-0.248	3 2 1
5	H	1.080	112.21	120.75	3 2 1
6	H	1.080	112.04	238.85	3 2 1
7	H	1.080	113.70	117.68	2 3 4
8	H	1.080	113.73	241.57	2 3 4
9	H	1.476	95.96	180.58	1 2 3
10	H	1.476	122.05	83.72	1 2 3
11	H	1.476	122.89	277.32	1 2 3

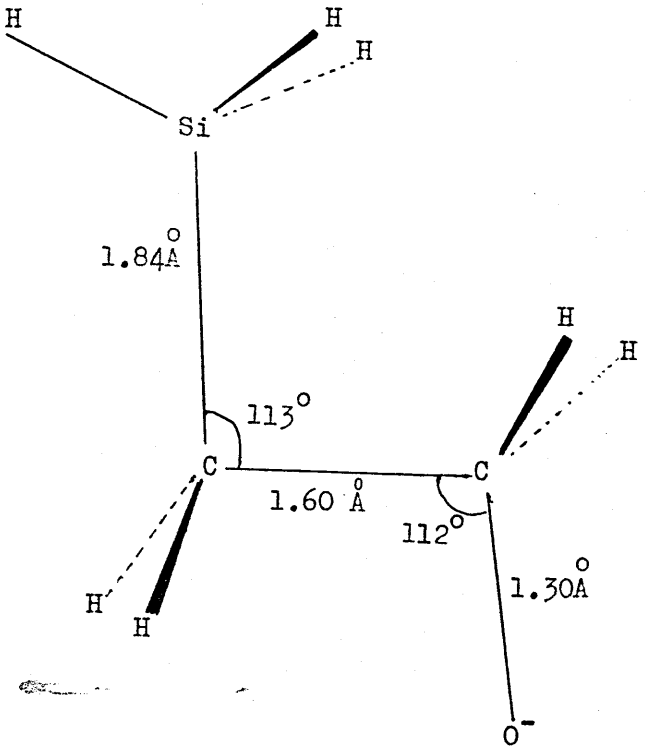
Table 20. Bond Lengths and Bond Angles of the Antiperiplanar Conformation

Atom Number I	Type of Atom	Bond Length (Angstroms) JI	Bond Angle (Degrees) KJI	Twist Angle (Degrees) LKJI	J K L
1	Si				
2	C	1.8462			1
3	C	1.604	112.89		2 1
4	O	1.300	113.62	179.19	3 2 1
5	H	1.080	104.09	53.05	3 2 1
6	H	1.080	103.98	305.04	3 2 1
7	H	1.080	109.96	58.95	2 3 4
8	H	1.080	109.92	299.56	2 3 4
9	H	1.476	112.65	179.82	1 2 3
10	H	1.476	115.38	61.24	1 2 3
11	H	1.476	115.29	298.45	1 2 3

Figure 2.



Synperiplanar Conformation
Enthalpy of Formation =
$-302 kJmol^{-1}$



Antiperiplanar Conformation
Enthalpy of Formation =
$-199 kJmol^{-1}$

The results of the MNDO calculations show that the Enthalpy of Formation of the synperiplanar intermediate is $-302 kJmol^{-1}$ whereas the Enthalpy of Formation of the antiperiplanar intermediate is only $-198 kJmol^{-1}$. Fig. 2, shows that the silicon-carbon-carbon bond angle is 89° in the synperiplanar intermediate but 113° in the anti-periplanar intermediate. The silicon oxygen distance is also quite close at 1.75 Å compared with 1.63 Å for a silicon oxygen bond. Thus, these calculations do indicate that silicon oxygen interaction may be an important factor in determining the conformation of the intermediate β-silyl alkoxide. Graph 1, also shows a transition state when the carbon atoms are separated by 2.6 Å. However, it is not possible to draw any definite conclusions from these results since the energies of the two transition states are very similar and also only a model α-silyl carbanion is under consideration in these calculations.

To gain further insight into the effect of silicon oxygen interaction on the stereochemistry of the Peterson reaction, experiments were performed in which electron withdrawing or donating groups were placed on the phenyl rings attached to the silicon. These results are illustrated in Table 21.

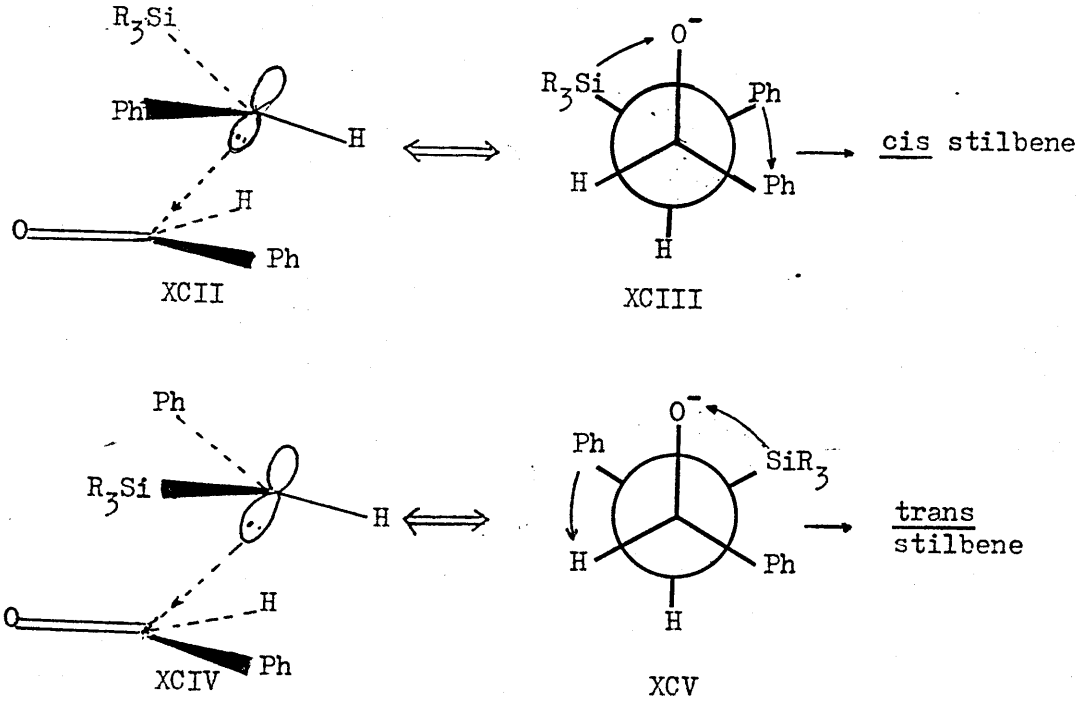
Table 21. The effect of electron withdrawing and donating substituents on the diastereoisomeric ratio of stilbenes produced by the Peterson Reaction

Nature of α-silylbenzyl carbanion prepared $PhC\bar{H}SiAr_3\ K^+$

The nature of the groups attached to the silicon atom	% Yield	Ratio of stilbenes (cis:trans)
Ar = $PhCF_3$-p	98%	1:1.22
Ar = PhF-m	95%	1:0.88
Ar = Ph	98%	1:0.55
Ar = PhMe-p	97%	1:0.64
Ar = PhOMe-p	100%	1:0.66

From these results there appears to be a general trend that placing electron withdrawing groups on the phenyl rings resulta in an increase in the proportion of trans stilbene produced. A possible explanation for this result is illustrated by Scheme 14.

Scheme 14.



Placing electron withdrawing groups on the phenyl rings would be expected to reduce the electron density on the silicon atom and cause greater attraction between the silicon and oxygen. If the reactants combine in the manner shown by XCII, increased attraction between the silicon and oxygen atom in the transition state results in the phenyl rings becoming unfavourably eclipsed as shown in XCIII. However, if the reactants combine in the manner shown by XCV, this interaction between the phenyl rings does not occur. Hence, when electron withdrawing groups are attached to the silicon atom and attraction between the silicon and oxygen atoms increases, the transition state XCIV has a lower energy than XCII. This results in an increased proportion of trans stilbene being produced.

Another possible clue to the degree of silicon oxygen interaction can be obtained by comparing the results given in Table 22.

Table 22. The effect of using a t-butyldiphenylsilyl or triphenylsilyl group on the diastereoisomeric ratio of stilbenes produced by the Peterson Reaction

Nature of the α-silylbenzyl carbanion prepared $PhC\bar{H}SiR^1R^2R^3\ M^+$

Nature of groups attached to the silicon atom	% Yield	Ratio of Stilbenes cis:trans
$R^1=R^2=Ph, R^3=\ ^tBu$	96%	1:0.65
$R^1=R^2=R^3=Ph$	96%	1:0.55

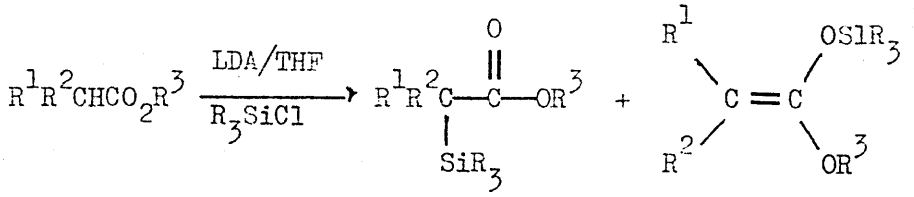
These results show that replacing a sterically bulky tertirary butyl group with a smaller phenyl group results in a small but

measurable increase in the proportion of cis stilbene being produced. This is a trend which would not be expected according to the mechanism proposed in Scheme 11.

One possible explanation for this result may be that the presence of the third phenyl group about the silicon atom reduces the interaction between the silicon and oxygen atoms in the transition state.

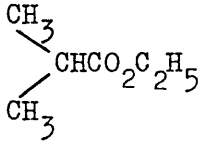
This results in an increased proportion of cis stilbene being produced via XCII. The effect of phenyl groups attached to silicon on the interaction between silicon and oxygen has been investigated by Lawson.[127] Some of the results are given in Table 23.

Table 23 The reaction of Lithium Ester Enolates with Chlorosilanes

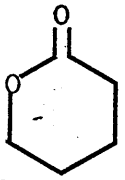


C-silylation O-silylation

Chlorosilane used = Me_3SiCl[128]

Ester used	% C-silylation	% O-silylation
$^nC_5H_{11}CO_2C_2H_5$	5	95
	< 1	99
$CH_3CO_2CH_3$	35	65
$CH_3CO_2C_2H_5$	40	60
$CH_3CO_2C(CH_3)_3$	98	2

Chlorosilane used = $MePh_2SiCl$

Ester used	% C-silylation	% O-silylation
$CH_3CO_2{}^tBu$	91	-
CH_3CO_2Et	93	-
CH_3CO_2Et	93	-
	94	-

These results show that when chlorotrimethylsilane is used to silylate lithium ester enolates, O-silylation predominates except when a tert-butyl ester is used. This latter is believed to be due to steric crowding at the oxygen enabling C-silylation to become preferable. With chlorodiphenylmethylsilane as the silylating agent, C-silylation occurs exclusively in every case. This difference in the regiochemistry between the diphenylmethylsilyl group and the trimethylsilyl group is thought to be due to the diphenylsilyl group being a softer electrophile. Hence, it becomes more reactive towards the carbon rather than the oxygen of the lithium ester enolate. This softening of the diphenylmethylsilyl group is thought to occur because the aryl groups donate electron density to the silicon atom via $p_{\pi}-d_{\pi}$ overlap.[129,130] The possibility that a steric effect is being observed is unlikely since the silylation reaction with chlorodiphenylmethylsilane is essentially quantitative and much faster than reactions using tert-butyldimethylchlorosilane.[131] To determine how the presence of phenyl rings may affect the stereochemistry of the Peterson reaction, experiments have been performed in which one or two phenyl rings are attached to the silicon atom. A full comparison of the results is given in Table 24.

Table 24 The effect of Phenyl group attached to the silicon atom on the diastereoisomeric ratio of stilbenes produced by the Peterson Reaction

Nature of α-silylbenzyl carbanion prepared $PhC\bar{H}SiR_1R_2R_3$

Nature of groups attached to the silicon atom	Alkoxide used to generate the α-silyl carbanion	% Yield	Ratio of Stilbenes (cis:trans)
$R_1=R_2=R_3=Me$	NaOSiMe	98%	1:1.30
$R_1=R_2=Me, R_3=Ph$ a	KO^tBu	97%	1:1.29
$R_1=R_2=Me, R_3=Ph$ b	KO^tBu	97%	1:1.29
$R_1=R_2=Ph, R_3=Me$	$NaOSiMe_3$	98%	1:1.39
$R_1=R_2=R_3=Ph$	$NaOSiMe_3$	102%	1:0.58

a = α-silyl carbanion generated from $PhCHSiMe_2Ph$ (SiMe$_3$)

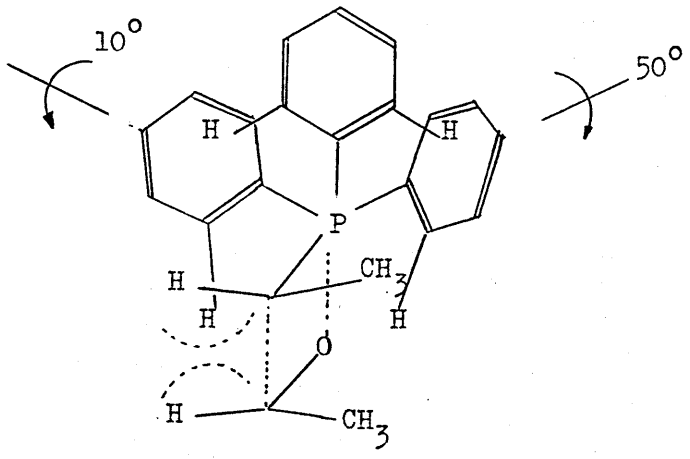
b = α-silyl carbanion generated from $PhCHSiMe_2Ph$ ($SiMe_2Ph$)

(The two experiments a and b had to be carried out as the potassium tert-butoxide attacked the dimethylphenylsilyl group as well as the trimethylsilyl group).

These results show that the presence of one or two phenyl rings has very little effect on the cis:trans ratio of stilbenes, relative to the result obtained with three methyl groups attached to the silicon atom. The major change in the cis:trans ratio of stilbenes

is observed when three phenyl rings are used. This indicates that the presence of one or two phenyl rings attached to the silicon atom may only have a small effect on the degree of silicon oxygen interaction in the transition state. It appears therefore that the results in Table 23 may be due to a special effect associated with the presence of three phenyl rings.

Schlosser[132] proposed a mechanism for the salt-free Wittig reactions which may account for the results given in Table 23. In this proposal it is believed that steric interactions in the transition state XCVII leading to oxaphosphetane formation determine the stereochemistry of the product olefins.



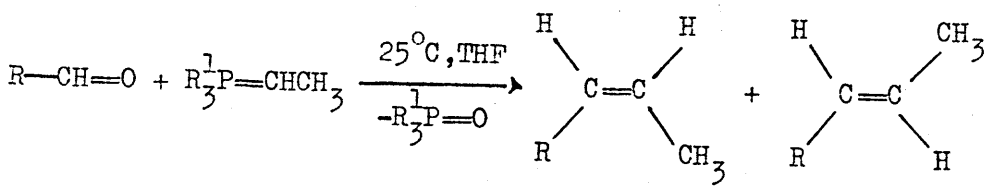
XCVII

In this transition all three phenyl rings are thought to be immobilized.[133] The methyl groups of the phosphorus ylid force the neighbouring phenyl ring out of the phosphorus trigonal basal plane by 50°. The axial phenyl ring is confined to a perpendicular orientation with respect to the developing four membered oxaphosphetane

ring. The third phenyl substituent is believed to be twisted out of the pyramidal plane (by roughly 10°) and is orientated with one ortho hydrogen close to the hydrogen associated with the attacking aldehyde. Thus any bulky group on this face of the incipient oxaphosphetane ring must cause serious steric repulsions. In contrast, on the opposite side, the methyl group of the aldehyde may approach the ylid side chain in a cis manner since the neighbouring phenyl ring will not interfere.

If this proposal is correct, ylids with less sterically demanding "stationary groups" should no longer exhibit cis but rather trans selectivity. This indeed was found to occur when ethylidenetriethylphosphorane was reacted with a series of aldehydes. A comparison of the results of Wittig reactions between aldehydes and ethylidenetriphenylphosphorane or ethylidenetriethylphosphorane is given in Table 25.

Table 25 The effect of changing the groups about the Phosphorus atom on the Stereochemistry of the Wittig Reaction.[132]



	Yield,% (cis:trans)	
	R^1= phenyl	R^1= ethyl
R= hexyl	95 (86:14)	94 (33:67)
R= tert-butyl	92 (98:2)	92 (10:90)
R= phenyl	94 (87:13)	99 (17:83)
R= p. chlorophenyl	88 (88:12)	89 (4:96)

Whether this proposal is applicable to the Peterson reaction depends upon how closely the transition state shown in XCVII resembles that of the Peterson reaction. In the salt-free Wittig reaction it is likely that a strong interaction exists between the positively charged phosphorus atom and negatively charged oxygen atom which results in the transition state having a synperiplanar conformation. However, in the Peterson reaction the silicon atom does not carry a positive charge and therefore a synperiplanar transition state would not be favoured. Also placing electron withdrawing or donating substituents on phenyl groups alters the cis:trans ratio of stilbenes produced. If Schlosser's proposal was strictly applicable to the Peterson reaction this variation would not have been observed.

3.9 Conclusion

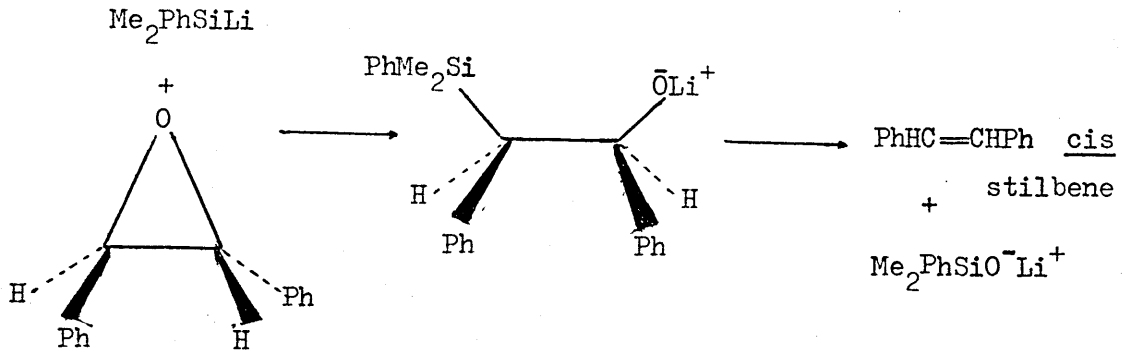
From the results of this project it is possible to draw certain conclusions about the reaction system that has been studied. The stereochemical outcome of the Peterson reaction is virtually unaffected by the use of lithium, sodium or potassium as the positive metal counterion to the α-silylbenzyl carbanion. The stereochemistry of the Peterson reaction is also unaffected by being carried out at different temperatures. Changing the solvent in which the reaction is performed or the addition of inorganic salts such as lithium iodide, lithium perchlorate or sodium tetraphenylboron, also results in only a very small change in the cis:trans ratio of stilbene products.

The addition of magnesium iodide to the reaction mixture or to a solution of preformed α-silylbenzyl carbanion does result in an increase in the proportion of trans stilbene being produced. However,

the yields of these experiments were low and it is difficult to draw any definite conclusions from the results obtained.

It has been shown that the stereochemistry of the Peterson reaction is determined by the initial combination of the reactants. This is known because the reaction between dimethylphenylsilyllithium and trans stilbene epoxide gives solely cis stilbene.[119]

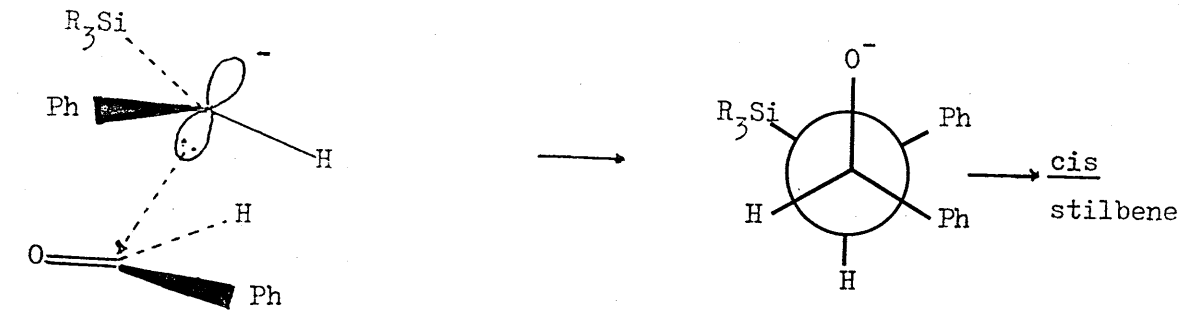
Scheme 14.



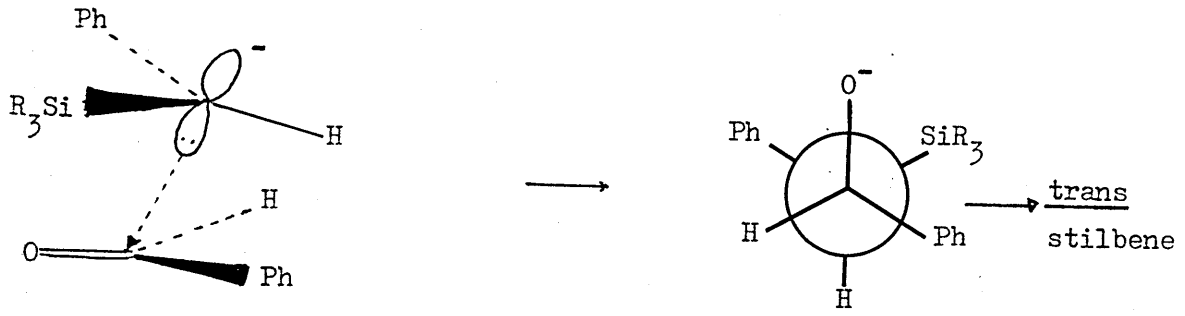
This shows that the intermediate produced undergoes stereospecific syn elimination of silanolate to give cis stilbene. It also shows that the stereochemistry of the product olefin is ultimately determined by the stereochemistry of formation of the intermediate and not by the mode of decomposition of the intermediate.

It has also been shown that placing sterically bulky groups about the silicon atom increases the proportion of cis stilbene. This is thought to be due to the reactants combining in the manner shown by XCVIII rather than XCIX as illustrated in Scheme 15.

Scheme 15.



XCVIII



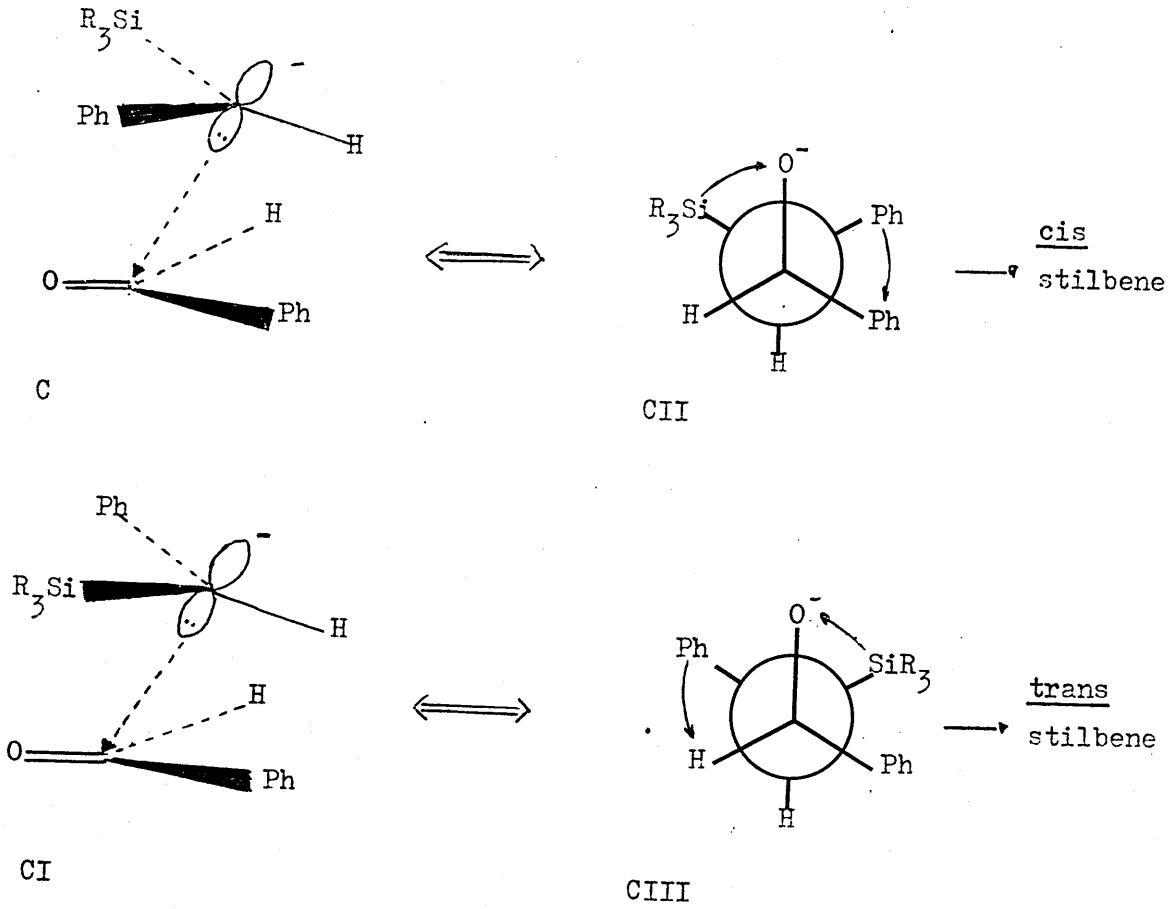
XCIX

In XCVIII the main steric interaction occurs between the phenyl ring of the benzaldehyde and the phenyl ring of the α-silylbenzyl carbanion. However, in XCIX the major interaction occurs between the silyl group and the phenyl ring. Hence increasing the steric bulk of the silyl group results in an increase in cis stilbene being produced.

Finally experiments have been performed in which electron withdrawing or donating substituents were attached to the phenyl groups about the silicon atom. The results of these experiments showed that placing electron withdrawing substituents on the phenyl rings resulted in an increased proportion of trans stilbene being produced. This is believed to be due to a greater silicon oxygen interaction in the transition state which leads to the threo intermediate being favoured. The erythro intermediate is not favoured owing to steric interaction between the

phenyl rings in the transition state CII. This is illustrated in Scheme 16.

Scheme 16.



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